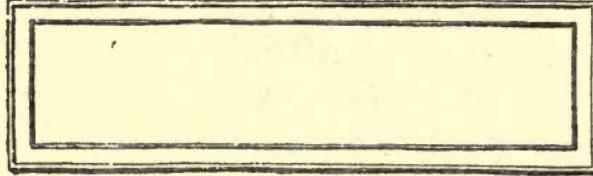
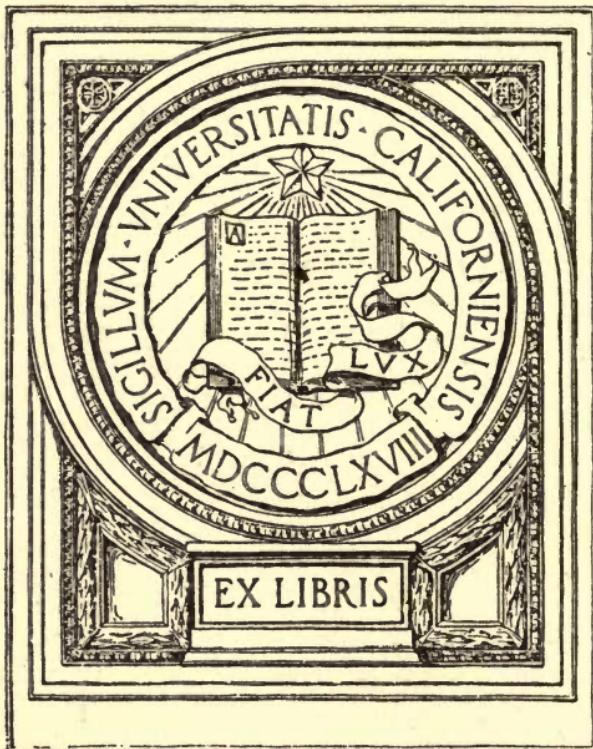
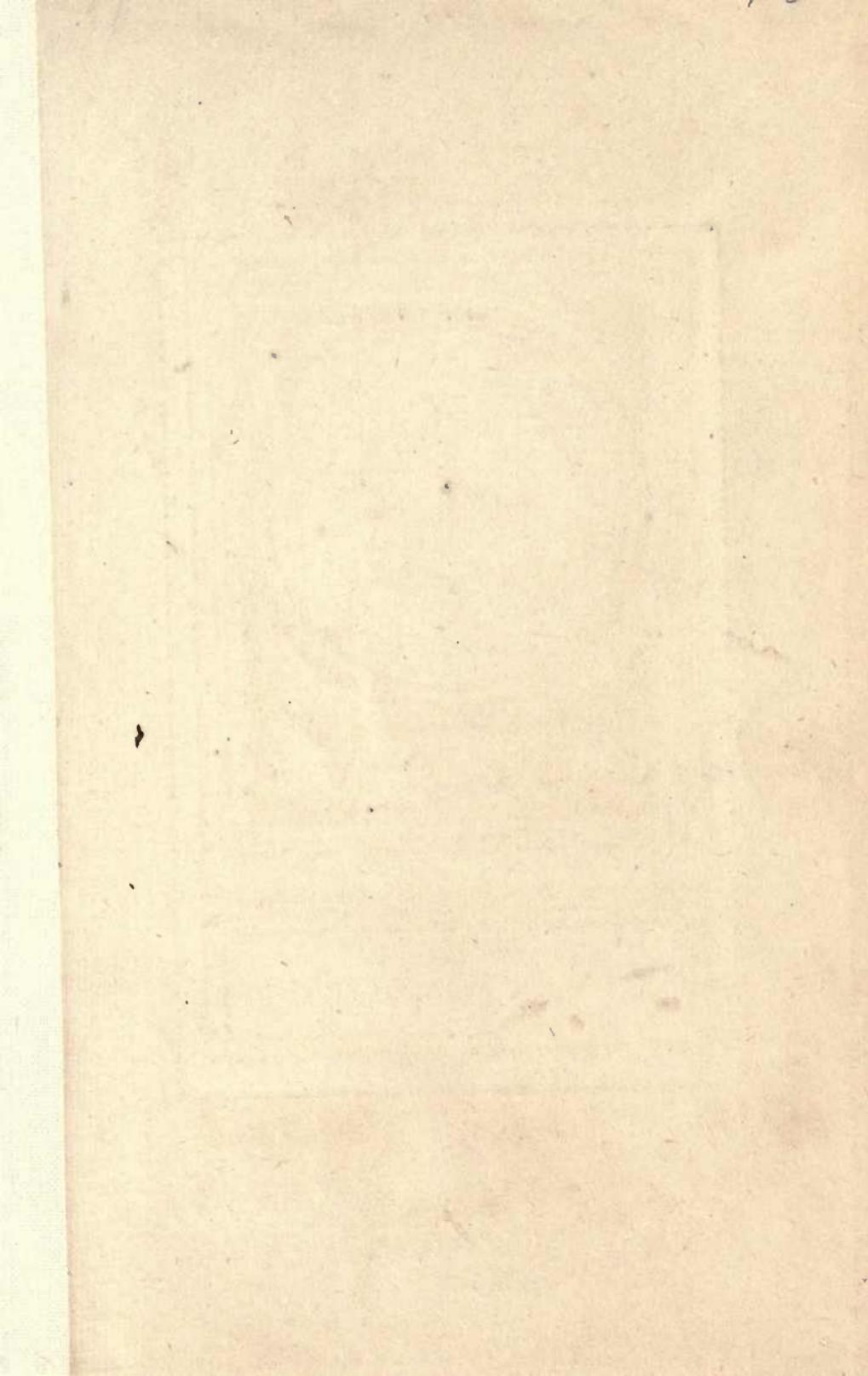


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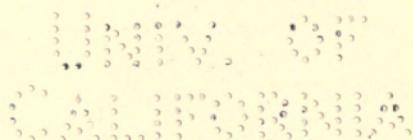
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BY

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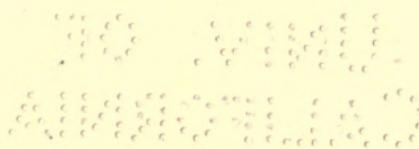
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NOTABLE VICTORIES

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CRIMES AGAINST HUMANITY

PERIODIC DISASTERS

PREFACE

IN these pages an attempt is made to give the specialized practical information—at least in broad outlines—required by chemists of sound general training who may be called upon, in whatever capacity, to deal with india-rubber and its accessories. The botany and theoretical chemistry of india-rubber, with which it has become almost common form to embellish all books on the subject, are here barely mentioned. More reluctantly, two important branches of science applied to india-rubber, viz., the production of the raw material and the mechanical testing of manufactured rubber, have also been passed over, mainly because they are as yet in the mere beginnings of giving rise to systematic laboratory practice.

There are two kinds of analytical text-book, the more or less exhaustive and less or more critical compilation from literature, and the strictly practical (and inevitably somewhat biassed) manual based on personal experience. Which of the two is the more valuable is a debatable point; and indeed they are rather complements than competitors. The present work, at any rate, claims in all modesty to belong to the second category, no analytical

method being described in it which has not been practised and found satisfactory by the author, in the course of the last ten years. If thus some information of value to the rubber chemist fails to find a place, it may be hoped, on the other hand, that the minimum of space is taken up by matter which time and experiment have proved otiose.

W. A. C.

LONDON, Dec. 1913.

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INDIA-RUBBER LABORATORY PRACTICE

CHAPTER I

CRUDE AND WASHED RUBBER

THE raw material which forms the basis of the rubber industry is a gum imported from the tropical regions of Asia, Africa, and America. Most of it is obtained primarily in the form of an aqueous emulsion or *latex* secreted by the bark of certain trees and creepers ; from this latex the rubber is won, as a tenacious, springy, self-adhesive mass, by methods of coagulation which vary somewhat widely with botanical origin, local custom, and other factors. In a few instances (notably that of Guayule, a Mexican sort), the rubber as such is directly extracted from roots and other plant parts. Rather more than half the total production of rubber originates from plants growing wild, and this "wild" rubber, which is almost the only kind produced in America and Africa, is always more or less moist, dirty, and inhomogeneous. The

imports from Asia nowadays consist for the greater part of clean dry rubbers prepared by rational methods on plantations organized and managed by Europeans in Ceylon, the Malay Peninsula, the Malay Archipelago islands, and India. At the same time, plantation rubber is now also being produced in East and West Africa, whilst Asia continues to export a certain amount of wild rubber.

Wild rubbers arrive in a great variety of forms, such as *sheets*; *blocks* or *slabs* composed of sheets; *balls* ranging in size from a fives ball to a large gourd and composed either of stratified concentric layers or of wound cord; *spindles*, *thimbles*, *spiral twists*, etc.; and *scraps* of irregular size and shape, which represent the offal of larger pieces and may be either loose, or compressed into blocks, or sewn into bags. Each sort of rubber has a characteristic and more or less powerful odour, which may be due to resinous constituents, decaying albuminoids, or foreign matter introduced in the preparation. Wild rubbers are usually soiled with vegetable refuse and earthy impurities and in addition contain amounts of moisture which may rise to 50 per cent. or over. In the manufacture of rubber goods, the crude wild rubber is first of all subjected to processes of washing and drying whence it emerges in the form of corrugated sheets or *crapes* (also spelled *crepes*) which are light grey when wet and dark grey or brown when dry. The percentage diminution of weight undergone by crude rubber as the result of this treatment is known as *washing loss*; it represents the moisture, dirt, and (almost, but not completely) the soluble non-rubbers originally present, and its amount, needless to say, is of high commercial importance.

Plantation rubbers are produced on well-organized and scientific lines, and leave little to be desired on the score of purity. As a rule they are sufficiently free from moisture, dirt, and albuminous matter to require no washing in the factory. They appear on the European markets in the form of *sheets*; *biscuits* resembling teacakes; *crapes*; or translucent *blocks*. The colour is mostly light yellow and the odour sweetish and very faint. *Smoked sheet and crape* have a dark red colour and a pronounced smoky smell.

Chemically, crude rubber is composed of rubber proper (rubber hydrocarbon), resin, moisture, dirt, albuminoids or "protein," and soluble organic substances of the nature of carbohydrates and tannins. The four last-named impurities are removed in the washing and drying operations, and constitute washing loss. Speaking generally, and leaving out of account physical and vulcanizational properties, it suffices for purposes of technical analysis to determine total washing loss and, in the thoroughly washed and dried material, the proportion of resin to true rubber and the ash. At the same time, occasions when more detailed analyses are desirable arise frequently enough, notably in the case of abnormal or unfamiliar rubbers.

Now crude rubber, especially when it takes the shape of large compact masses, is such a very inhomogeneous material that correct sampling is a matter of no small difficulty. The only really accurate way, therefore, of ascertaining washing loss is from the weights recorded in the factory process itself, where batches of the order of a hundredweight are worked up. But the problem which commonly confronts the chemist is that of determining washing loss upon a comparatively small sample. This

is done in the laboratory by means of a miniature washing mill and drying oven, and is in itself an operation admitting of high precision. If a definite hand-sample of crude rubber should be submitted, then the whole of the sample is thus dealt with, and the chemist's responsibility is limited to carrying out the assay correctly. When, on the other hand, a large quantity of rubber has to be reported upon, much care and judgment must be exercised in drawing as representative a sample as possible. Generally speaking, rubbers in small pieces can be far more accurately sampled than those which are in large masses, because the former are usually comparatively dry, whereas the moisture content of the latter is very unevenly distributed.

A ten to twenty pound lot of crude rubber should be drawn for experimental washing, and should be immediately wrapped in oilcloth or rubber sheeting pending treatment, so that evaporation of moisture may be reduced to a minimum. The following modes of procedure, modified in such ways as the sampler's judgment may suggest, are to be recommended for sampling from bulk :—

If the consignment consists of more than one cases or bales, it is best to take one sample from each. Should there be many packages, the contents of which seem much alike on inspection, a sample may be taken from every second or third package. Each sample is assayed separately for washing loss, and the arithmetical mean is taken. Aliquot parts of each washed lot are then mixed on the rollers to form a single sample on which the further analysis can be conducted.

The whole contents of a package should be turned out on the floor and inspected. If the rubber is in the form

of fairly regular small pieces, sampling is comparatively easy: pieces of normal appearance are picked from various places all over the heap until the required quantity is made up. If the pieces are balls of medium (and possibly varying) size, a representative collection, amounting to more than the sample quantity, is first made, and the sample is then reduced to convenient weight by halving or quartering each ball.

In the case of small scrap, the bulk should be classified by eye into a few dominant categories according to size and shape, and specimens of each picked in due proportion.

Large balls, slabs and sheets are more difficult to sample. Usually the outside is the dirtiest and driest portion, moisture and with it the soluble constituents being concentrated inwards; often a white, dripping wet core is concealed by a dark dry exterior. There will not be many large balls or ball segments in one package, and the safest plan is to cut a proportional fragment from each. The correct sample to take from a ball is a wedge with its apex at the centre. The cutting is performed with a long-bladed knife or toothless saw. A half-ball, *i.e.*, a hemispherical piece, may be sampled by cutting out a parallel-sided slice through the middle.

With sheet and slab rubber also, it is best to cut a portion from each slab or agglomeration of slabs that is covered all over with a dark crust. A slice or rasher cut diagonally from corner to corner of a rectangular slab represents the best average; but it does nearly as well, and is less troublesome, to cut a rasher right through the middle, at right angles to the longer side of the slab. The bulk of each slice should be roughly proportioned to that of the slab itself, and total weight may afterwards be reduced, if necessary, by halving.

Details of the process of determining washing loss are given in the next chapter (p. 21). Washing losses and other analytical data for the chief types of crude rubber are tabulated in the Appendix (p. 181).

When it is desired to make an analysis of crude rubber before it has been washed, a suitable sample, which may be much smaller than a washing sample, is dried in the vacuum oven and is subsequently mixed to a homogeneous sheet on the hot rollers. This method is by no means to be recommended for crude rubber analysis generally, but may often prove serviceable in the absence of a washing mill, or when the rubber is not intended to be washed on the large scale.

Plantation rubbers, in the nature of things, are mostly quite uniform for a given consignment from one estate, and seldom contain more than one or two per cent. of moisture, dirt being practically absent. There is rarely need, therefore, for extra care in sampling, or indeed for washing. Unless obviously wet or dirty, plantation rubbers may be regarded as ready for chemical examination without preliminary treatment.

Analysis of Crude or Washed Rubber.

1. *Moisture.*—The most satisfactory method of determining moisture consists in heating 5–10 gr. of rubber, cut into snippets and laid on a flat porcelain dish, in a laboratory vacuum-oven (see p. 23). Factory-dried rubber requires about two hours, being already not far from anhydrous; damp material such as unwashed crude rubber should be heated until the weight is constant, and may require a day or more. Unvulcanized rubber of the better sort, being less prone to oxidation than vulcanized, may indeed be dried in an ordinary air-oven without

serious error, provided the operation be conducted expeditiously. Flabby or resinous sorts, however, are best dealt with *in vacuo* at a temperature of about 60°. Drying over sulphuric acid in a vacuum-exsiccator is an excellent method, but far too tedious, since it always requires days and sometimes weeks.

2. *Resin*.—In rubber generally, whether vulcanized or not, resin is determined by extraction with boiling acetone. This is carried out by means of a Knöfler extractor, which acts intermittently on the Soxhlet principle whilst surrounding the centre of extraction with acetone vapour (*cf.* Fig. 13). For raw rubber analyses the inner tube may with advantage be about 25 mm. wide, with a siphoning height of about 8 cm.; a filter-thimble may be dispensed with. The rubber should be cut up into cubes of about 2 mm., but very thin crapes may be extracted without previous comminution, if only they are rolled up loosely enough to provide circulation-space within the spiral. Soft resinous rubbers are apt to run together in the extractor and so prevent complete extraction. In such cases the original snippets may be spread on a sheet of muslin which is then rolled into a spiral. Or again, the snippets may be extracted as usual and the sintered lump dried, cut up afresh, and re-extracted.

Of Brazilian and plantation rubbers not less than 10 gr. should be weighed out; of African sorts, Borneo, Guayule, &c., 5 gr. will suffice. A duration of ten hours is ample for complete extraction. The acetone solution is then distilled nearly dry on a water-bath and heated for three hours in an air-oven at 110°, by which time the weight of the residue, unless there be an unusually large amount of it, will be constant. Fluid resins of the Brazilian and plantation types give off volatile matter at 110° and never

attain real constancy, but three hours is a useful conventional drying period to apply to them.

With the majority of crude rubbers a certain amount of carbohydrate matter (mainly sugars of the inosite class) will be found in the extract. This impurity, though freely soluble in water, is seldom completely got rid of in washing the rubber, and may make up as much as 5 per cent. of the acetone extract. It is only sparingly soluble in acetone, and generally gathers into a white subcrystalline ring near the top of the extraction-flask; a separation from resin proper may easily be effected by means of chloroform, but as a rule there is no harm in weighing the carbohydrate as part of the resin.

3. *Ash*.—Of the roughly cut up material 5 gr. are weighed in a flat porcelain dish and gently heated to fusion and decomposition. It is well not to allow the vapours to kindle; if nevertheless they should take fire, the flame should be extinguished by an improvised lid of sheet metal or asbestos. Royal Berlin porcelain dishes are the best to use, as being little liable to crack on heating. After the bulk of volatile matter has been driven off, the dish is heated to redness in a muffle until all charred matter has disappeared.

The ash of washed and plantation rubber ranges from 0·1 to 1·5 per cent., rising exceptionally to 4 or 5 per cent. In most cases the ash is white or pale yellow and infusible, and consists mainly of silica, lime, and magnesia. A few rubbers give ashes so highly ferruginous as to be of brick-red colour. The ash content of a rubber is significant (1) as an item in the non-rubbers and (2) as a check on the effectiveness of washing operations. Occasionally it may prove useful, qualitatively and quantitatively, for characterizing the species and botanical origin of a rubber.

4. *Proteid and other Nitrogenous Matter.*—Direct determinations of protein in rubber cannot be made: indeed it is not yet known what the nature of rubber protein is. The usual custom is to determine total nitrogen and to multiply by the conventional factor 6·25. Kjeldahl's method of nitrogen assay is applied as follows:—

Two gr. of rubber are placed in a 100 c.c. long-necked decomposing flask with 30 c.c. of concentrated sulphuric acid and a small drop (about 1 gr.) of mercury. The flask is loosely stoppered with a small funnel and heated over the naked flame. At first there is copious evolution of sulphur dioxide, and the flame must be cautiously regulated. Later on, the dark liquid is heated to vigorous ebullition. After five or six hours the liquid will usually have become straw-coloured, beyond which point it is needless to go. Should there be any difficulty in reaching straw-colour, the cooled liquid may be treated with a little permanganate and boiled up afresh. The residue is now cautiously diluted and rinsed into a large flask; one or two gr. of sodium sulphide, an excess of caustic soda solution, and a few scraps of zinc are added. The ammonia is distilled, with the usual precautions, into 20 c.c. of $N/5$ sulphuric acid, which are subsequently titrated back with $N/5$ alkali and methyl orange.

5. *Insoluble Matter*, i.e., matter insoluble in rubber solvents. This includes all such mechanical impurities as sand, clay, woody fibre, humus, &c., but not the whole of the nitrogenous nor of the colouring matter. As a rule it includes slightly less than the total ash, part of the inorganic matter being present as salts of calcium and other metals soluble in organic solvents. The determination of insoluble would be easy enough if it were not for the extreme viscosity of rubber solutions and the presence

of part of the rubber in a pectous modification not directly soluble in cold solvents. With some few low-grade rubbers, simple dissolution, filtration, and washing of the residue are practicable within reasonable time. In general, however, it is necessary to begin by applying heat treatment to the rubber. The three following methods are available :—

1. Where mixing rollers are at hand, a quantity of the rubber is worked hot until plasticized, *i.e.*, until it can be drawn out in a uniform translucent sheet. The pectous part of the rubber is thus rendered soluble, and the resulting solutions are comparatively fluid. Two gr. of the prepared material are swelled overnight in 100 c.c. of toluene or solvent naphtha and dissolved by shaking. Should the solution still be too viscous to be manageable, it is now boiled under reflux condensation, by the aid of an oil-bath, for several hours. The liquid, when sufficiently deviscified, is allowed to settle and is filtered; or, far better, it is whirled in a centrifuge (see p. 27), when the insoluble goes to the bottom in so compact a form that the supernatant liquid can be simply poured off. The insoluble is best received on a tared ashless filter; for washing, there is no neater method than suspension in toluene vapour for an hour or so (see under "Gutta-Percha," p. 172). The weighed filter is incinerated and the ash is deducted. This gives *organic insoluble*, which is the true objective of the assay.

2. C. Beadle and H. P. Stevens¹ heat one gr. of finely-cut rubber in a test-tube with 5–10 c.c. of phenetol for several hours, first at 100°, then at temperatures rising to 140° or over. The thin solution is diluted with 100 c.c. of benzene and allowed to settle. The residue may be

¹ *India-Rubber Journal*, 43 (1912), p. 193.

filtered off, or it may be washed repeatedly by decantation, rinsed on to a tared dish, and dried.

3. In lieu of phenetol, petroleum may be used for obtaining thin solutions from unworked rubber, the procedure being exactly the same as that applied to vulcanized rubber (see p. 141). Two gr. are heated with 15 c.c. of petroleum (B.P. 200° upwards) in a small flask until reduced to a thick, but homogeneous, solution. Half an hour's heating at 200° generally suffices. After dilution with 100 c.c. of any convenient solvent, the insoluble is filtered off directly or after centrifugal treatment, and dealt with as under 1. On the whole, this method is the cheapest and most expeditious ; unlike the first two methods, however, it provides no possibility of simultaneously determining the rubber-substance which has gone into solution.

The following figures, obtained by method 3, give some idea of the amounts of insoluble that may be expected. They represent percentages upon washed dry material :—

Rubber Sort.	Acetone Extract.	Ash.	Total Insol.	Ash of Insol.	Organic Insol.
Para	3·04	0·26	0·50	0·10	0·40
Sernamby	1·84	1·27	1·55	1·05	0·50
Maniçoba	3·10	2·60	4·90	2·35	2·55
Guayule	29·40	2·36	4·35	2·10	2·25
Gaboon Ball	26·50	0·40	1·80	0·35	1·45
Borneo	8·92	0·37	0·50	0·10	0·40
Manihot Plantation	8·25	1·93	4·10	1·10	3·00
Malay Plantation Crape . .	3·30	0·30	1·10	0·25	0·85
Ceylon Plantation Biscuit .	2·87	0·40	1·80	0·25	1·55

6. *Rubber Proper*.—The most widely practised, and certainly the least troublesome, method of arriving at the percentage of true rubber hydrocarbon in unvulcanized

material is the simple process of subtracting the combined percentages of moisture, ash, organic insoluble, protein, and acetone extract from 100. For technical purposes it commonly suffices to subtract resin and ash only; but this involves a possible error of one or two per cent., and in the case of badly washed rubbers of several per cent.

In washed rubber the estimation of rubber hydrocarbon by difference from the fully determined non-rubbers is usually accurate to within one per cent., sufficiently, that is, for all ordinary purposes. When, as may sometimes be the case, it is inconvenient to determine all the non-rubbers, rubber proper may be determined directly, either as such (the determination is then in principle the same as that by difference) or in the form of a derivative. Direct determination is also to be preferred, as a rule, in the analysis of uncured doughs and rubber solutions.

Determinations in which the rubber is weighed as such may be carried out (1) by precipitation or (2) by evaporation:

1. A deviscified solution of one or two gr. of material in rather less than 100 c.c. of toluene is prepared as described under "Insoluble Matter" (p. 10). When cool, it is made up to 100 c.c. and allowed to settle completely; this may be accelerated by warming on a water-bath or by the aid of a centrifugal machine. Of the clear liquid 50 c.c. are pipetted off, and dropped into 100 c.c. of warm alcohol, which is kept in brisk motion the while. Rubber hydrocarbon is thus precipitated as a clot. Should there be present 10 or more parts of resin to 100 of rubber, the clot is redissolved and reprecipitated; if the proportion of resin be very high, a further reprecipitation is advisable. The clot is kneaded with several relays of warm alcohol, drained as far as possible, transferred to a tared dish,

dried to constant weight in the vacuum oven, and weighed.

2. Fifty c.c. of clear solution are pipetted off as above into a tared wide-mouthed flask of 100 c.c. capacity. The solvent is distilled off and the flask is cursorily dried in the vacuum oven. Alcohol is then added and the flask is set to boil for an hour under reflux, when the film of rubber detaches itself from the glass and gives up its content of resin to the alcohol. This treatment with alcohol is repeated three or four times, whereupon the liquid is drained off and the flask is dried to constancy in the vacuum oven and weighed.

Both these methods work better, as regards accuracy, the less resin there is present. With highly resinous rubbers it is preferable to begin by submitting the material to acetone extraction. If the extraction has been exhaustive, a single boiling out with alcohol will suffice in method 2; it is less safe to dispense with alcohol altogether, owing to the difficulty of driving off the last traces of original solvent. In this and all similar analytical processes it is well to weigh out original substance before extraction rather than to start from a weighed quantity of extracted material. Errors due to imperfect drying and to oxidation are thus avoided, and calculation is simplified.

Rubber can also be determined on the orthodox analytical principle of weighing the object of assay in the form of a derivative, which in this case is an addition-product, rubber tetrabromide. The rubber molecule, unfortunately, cannot be trusted to combine quite neatly with just four atoms of bromine per $C_{10}H_{16}$ radical, and there are questions with regard to the behaviour under bromination of proteins and resins, and the analytical decomposition of the

tetrabromide, which are not fully cleared up. Hence in point of accuracy determination as bromide has little or no advantage over determination as isolated rubber. Nevertheless, the tetrabromide method is not without its usefulness in emergencies. It is carried out (T. Budde's¹ method, modified by D. Spence and J. C. Galletly²) as follows :—

About 0·2 gr. of material is weighed out, extracted with acetone, covered in a wide-mouthed stoppered bottle with 50 c.c. of carbon tetrachloride, and allowed to swell overnight. Fifty c.c. of a reagent composed of 6 c.c. of bromine and 1 gr. of iodine in a litre of carbon tetrachloride are added to the solution and left to react for six hours with occasional shaking. The tetrabromide is precipitated by adding 50 c.c. of alcohol with constant stirring and is washed by decantation several times with alcohol. To remove the last traces of free bromine and foreign bromides, the drained precipitate is allowed to swell in carbon disulphide, reprecipitated by 50 c.c. of petroleum spirit, well washed with alcohol, and roughly dried at low temperature. Instead of being weighed as such, the tetrabromide is now transferred to a porcelain or metal crucible, where it is mixed and covered with about 4 gr. of a mixture of sodium carbonate and potassium nitrate (2 : 1). The crucible is heated to redness, but to a point just short of complete fusion. The contents are dissolved in the minimum of water, acidified with a decided excess of nitric acid, and well boiled. On cooling, the bromine is determined by adding an excess of N/10 silver nitrate solution and titrating back with thiocyanate solution in presence of iron alum. For converting the bromine thus

¹ *Gummi-Zeitung*, 24 (1909), p. 4.

² *Le Caoutchouc et la Guttapercha*, 8 (1911), p. 5513.

found into terms of rubber hydrocarbon, the factor 0·42 may be used.

General Remarks on Raw Rubber Analysis.

For the works control of crude wild rubbers it suffices to assay each consignment, after washing, for ash and resin. The ash-content is of interest with respect to the efficiency of the washing process; in special cases it may be desirable to determine insoluble as well. The efficiency of works drying ovens may be tested by determining moisture from time to time. Even the stickiest rubber can quite well be dried on the large scale to within 0·5 per cent. of moisture, and this should be set as an upper limit. Plantation rubbers are comparatively easy to control by simple inspection, and call for chemical examination only in exceptional cases. As for rubber "protein," that portion of it which remains after washing is practically inert and need not claim the regular attention of the laboratory.

The washing loss of crude rubber is of importance in regard to the price of the material, but has nothing to do with the quality of the rubber. For a given rubber sort it is, within easy limits, constant and therefore to a certain extent characteristic.

Resin-content varies between 1 per cent. and 30 per cent., but in a given rubber sort is constant within fairly close limits. South Americans as a class are mostly poor in resin: in *Hevea* rubbers it rarely exceeds 4, in *Manihot* rubbers 7 per cent. Plantation rubbers usually contain only 2—3 per cent., but young trees are apt to yield rather more resinous rubbers. From the manufacturing point of view it is by no means to be assumed that a rubber is better the less resin it contains: the wide variations in

the physical properties of the rubber hydrocarbon itself are of far greater import. At the same time, it does usually happen that rubbers associated with, say, 20 per cent. of resin are of poorer quality than rubbers associated with, say, 2 per cent., but even this mild generalization cannot be regarded as free from exceptions. In any case, resin is always a non-rubber and always a diluent, just as much as added pitch or wax would be. Further, when present in a large amount, rubber-resin is apt to exercise an unfavourable effect on vulcanization.

South American resins are generally liquid, dark in colour, and of an empyreumatic odour. Plantation resins are similar, but of a lighter colour. The majority of African resins are yellow, transparent, and brittle, but still capable of flowing slowly at ordinary temperatures. A very few resins (Gambia, certain Congos, Rambong, Penang, Java, &c.) are hard and pulverizable. Resins from Para and plantation rubbers are optically inactive, whereas most others show a moderate dextro-rotation.¹ A list of the resin-contents of various rubber sorts will be found in the Appendix, p. 181.

Nitrogen in crude unwashed rubber may amount to as much as 1 per cent. The usual practice of classifying the whole of this as proteid nitrogen and multiplying by 6·25 is open to question, but for the present there is nothing better to offer. A portion of the nitrogen certainly exists as albuminoids soluble in water, which are, or should be, completely removed by washing. It is this impurity which by its putrefaction gives rise to the evil odour emitted by some rubbers, and there is reason to believe that decay of the associated albuminoids has a

¹ F. W. Hinrichsen and J. Marcusson, *Z. Angew. Chem.*, **23** (1910), p. 49.

deleterious effect on the rubber itself. Hence in general it may be said that a crude rubber will keep better, the less nitrogen it contains. The only practicable method of determining soluble albuminoids is by the difference between nitrogen in the crude and nitrogen in the washed rubber, due allowance being made for washing loss.

The remainder of the nitrogen, which in extreme cases (notably in hard fine Para) may reach 0·4 per cent. of the washed dry rubber, appears to be a sign of strength rather than of weakness. In what form exactly it exists is not known, but it would seem to be closely bound up with that sometimes very considerable "pectous" portion of the rubber which swells up to a gel in rubber solvents without going into fluid solution.

The pectous rubber here referred to scarcely differs chemically from soluble rubber and becomes itself soluble when the material is subjected to hot rolling or other heat treatment. The expressions "rubber proper" or "rubber hydrocarbon" are to be taken throughout as connoting that which ranks technically as such, without regard to differential solubilities.

CHAPTER II

MACHINERY AND APPARATUS.

A LABORATORY in which the determination of washing losses is carried on will require a small washing mill and a vacuum drying oven. In addition, a small mixing mill is an exceedingly useful adjunct for general purposes. This and other machinery should be set up, preferably against an outside wall, in a soundly-floored room separate from the laboratory proper. The washing mill, moreover, should be screened off by itself, on account of the inevitable splashing. The drive is best conveyed from an overhead countershaft and may proceed from a small gas-engine, or better from an electric motor, of 2—5 H.P. Another plan, which is very convenient as regards control but involves rather more floor-space, is to drive each machine independently by an electric motor, copiously geared down. Roller mills should be lighted either from the top or from the side immediately opposite the operator.

Washing of Crude Rubber.—The process consists in squeezing the gum repeatedly through a pair of grooved rollers in a constant shower of cold water. Small-scale washing mills, which are practically identical in all but

size with the full-scale machine, are supplied to order by most of the rubber-engineering firms. For laboratory work the rollers, of solid chilled iron, may advantageously have diamond or spiral grooving more closely set and in

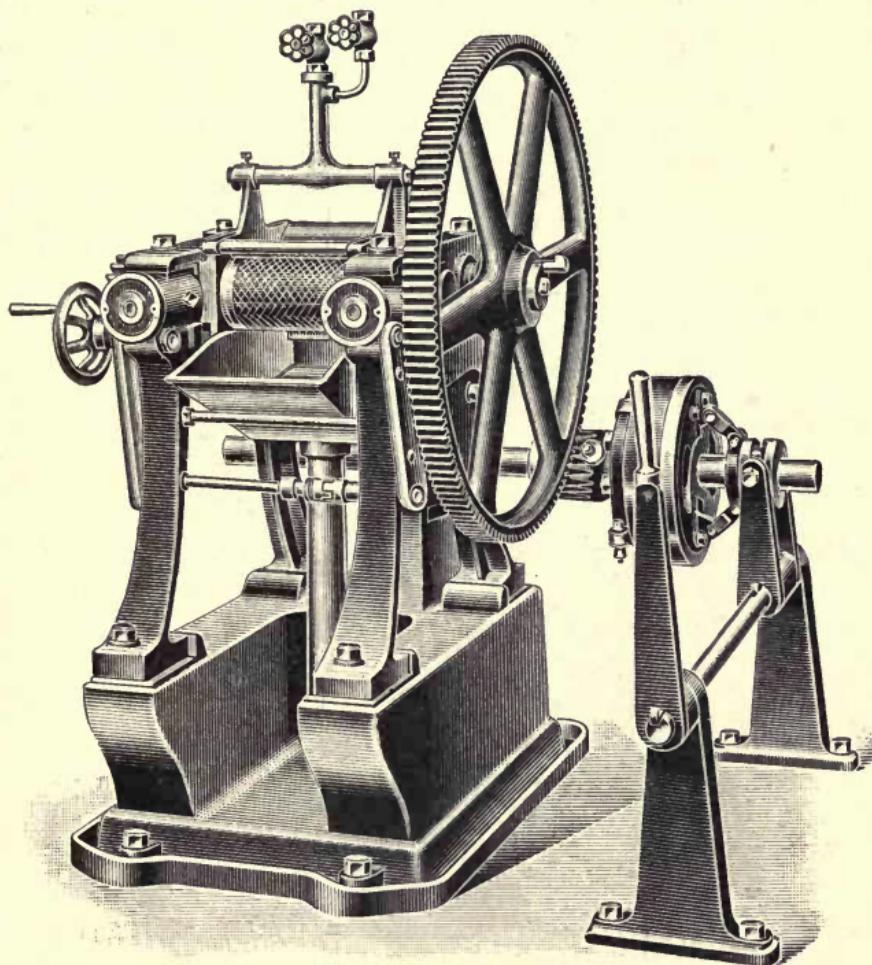


FIG. 1 (Scale 1:16).

shallower relief than on full-scale rollers. The floor-space taken up by such a mill, apart from motive machinery, may be from $2\frac{1}{2}$ to 3 feet square; the height of the rollers from the ground should be about 3 feet.

A laboratory washing mill¹ with rollers 9 in. long by 4½ in. diameter, is shown in Fig. 1; another, with rollers 12 in. by 6 in.,² in Fig. 2. It is quite feasible to wash

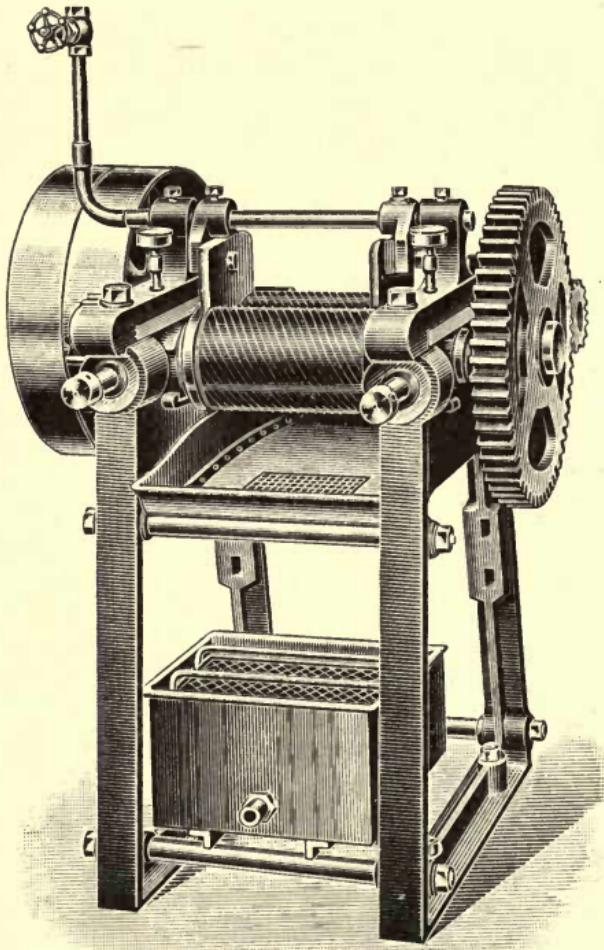


FIG. 2 (Scale 1 :15).

even very small batches of rubber on full-scale machines of the smaller kind as used in factory and plantation work.

¹ By Messrs. D. Bridge & Co., Manchester.

² By Messrs. J. Robinson & Co., Salford.

The weighed crude rubber is softened, if necessary, by steeping in hot water and is cut into pieces small enough to pass through the rollers without unduly straining them. The mill is set in motion, and a continuous spray of water is directed from above towards the space between the rollers. By sending it repeatedly through the rather widely spaced rollers, the whole of the batch is worked into a coherent sheet of sodden crape. This crape is then passed through again and again, the rollers being meanwhile screwed up gradually into closer contact, until at length the wash-water flows off colourless and free from suspended matter. The capacious pan which receives the wash-water must be fitted with a grid at its outlet: pieces of rubber which are carried away to this grid are recovered and added to bulk. The washed crape is eventually hung up to drain for an hour or two and is then ready for drying. The difference in weight between the original batch of crude rubber and the fully dried washed crape, calculated as a percentage of the former, represents washing loss.

Drying Ovens.—Washed rubber is dried in vacuum-ovens which may conveniently be miniatures of the vacuum driers in use on the large scale. A small drier of this sort¹ is shown in Fig. 3. The boiler-shaped drying chamber is closed by an hermetically-fitting door and contains three shelves, each of which is heated by means of steam-coils. A wide vacuum-pipe leads out of the chamber to a vertical condensing column, and this in turn is connected to a power-driven air-pump. By the arrangement of pipes shown in the figure, the shelves can be heated up by direct steam before evacuation, and thereafter by waste steam issuing from the air-pump. This

¹ By Messrs. Emil Passburg, Berlin.

drier has rather over 20 sq. ft. of floor-space on the shelving, and is therefore more especially suitable for laboratories in which a good deal of rubber-washing is continually going on.

Laboratory vacuum-ovens proper, of the type shown in Fig. 4,¹ are commonly horizontal jacketed copper cylinders,

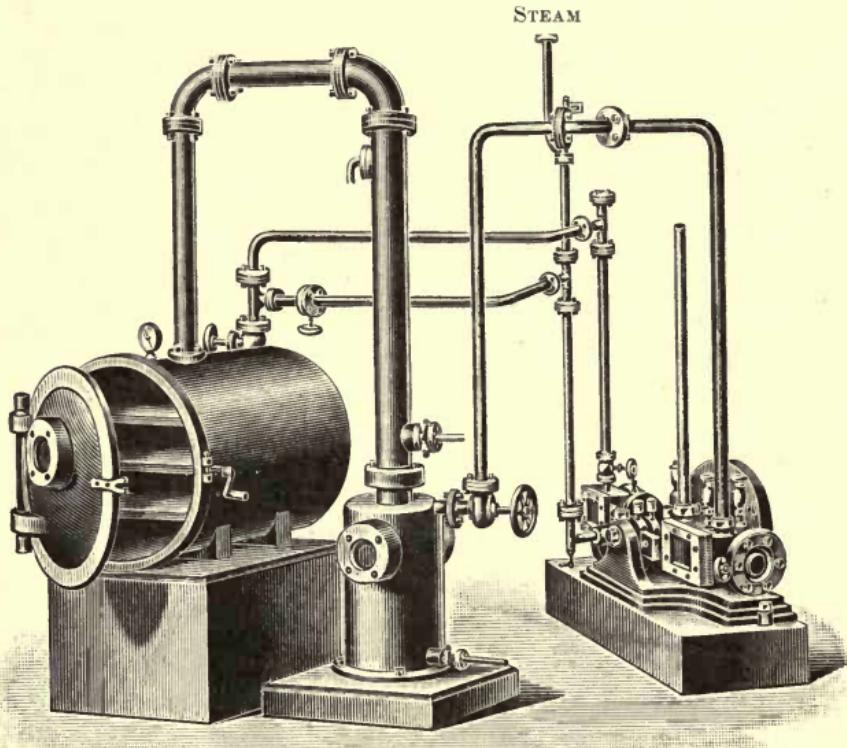


FIG. 3 (Scale 1 : 30).

capable of being heated either by steam or by gas-burners acting on a jacket of water or other liquid. They are obtainable in a wide range of sizes, from about three litres capacity upwards. Jacket-heating is not so efficient as shelf-heating, but the latter principle is not easy to apply to small drying chambers. The larger vacuum-ovens are

¹ By Messrs. A. Gallenkamp & Co., London.

best evacuated by means of a Geryk air-pump actuated by a small motor. For those of only a few litres capacity a metal filter-pump answers very well, given an ample and undisturbed head of water.

A small vacuum drying oven as in Fig. 4, is an exceedingly useful, if not indispensable, piece of labora-

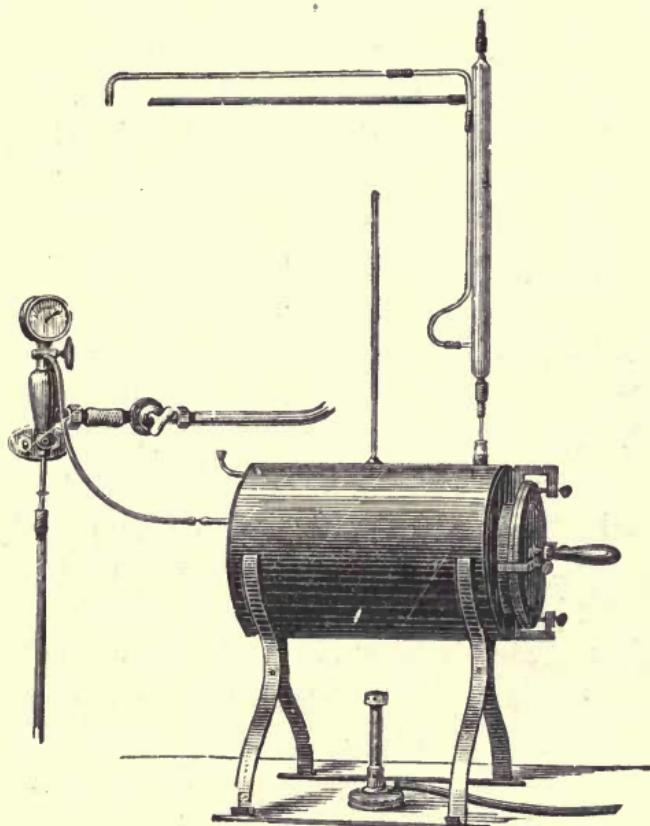


FIG. 4 (Scale 1:15).

tory apparatus for general analytical use in connection with rubber. The oven is here shown heated by means of a liquid boiling under reflux condensation; but low-pressure steam, wherever available, is more convenient. As regards *air-ovens* for ordinary laboratory purposes, it need only be remarked that 110° and 60° are the most

generally useful temperatures, and that the best mode of heating is by a directly impinging Bunsen burner governed by an ordinary mercury thermo-regulator.

Drying ovens through which a slow current of carbon dioxide or other indifferent gas is kept passing are capable of rendering very good service for drying small quantities of rubber or gutta-percha. Any small air-oven of which

the door and its frame are sufficiently robust to be made gas-tight by means of a rubber washer may thus be utilized. A makeshift, but quite efficient, small drier of this kind may be constructed from a laboratory vacuum-still consisting of a metal or porcelain pan and a glass dome (Fig. 5). Inside the pan, a disc of perforated brass or zinc rests, one or two inches from the bottom, upon a tripod. The pan is heated by a burner admitting of delicate regulation. A thick rubber or asbestos washer is interposed between pan and dome, which are clamped together by three small thumb-screws not shown in the illustration.

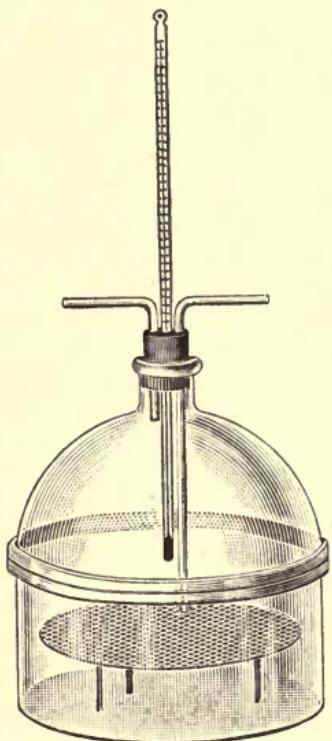


FIG. 5.

Roller Mills.—These serve (1) for comminuting rubber and other materials, and (2) for plasticizing, mixing, and sheeting unvulcanized rubber. Whilst similar in build to washing mills, they have smooth-faced hollow rollers capable of being water-cooled or steam-heated at will. Miniature mixing mills are supplied by rubber engineers

under the same conditions as miniature washers. Fig. 6 shows a heavy laboratory mill¹ fitted up with all the paraphernalia of a self-contained electrical drive, transmitted through a worm gear; the rollers are exceptionally stout, viz., 9 in. long by 8 in. diameter. An essentially

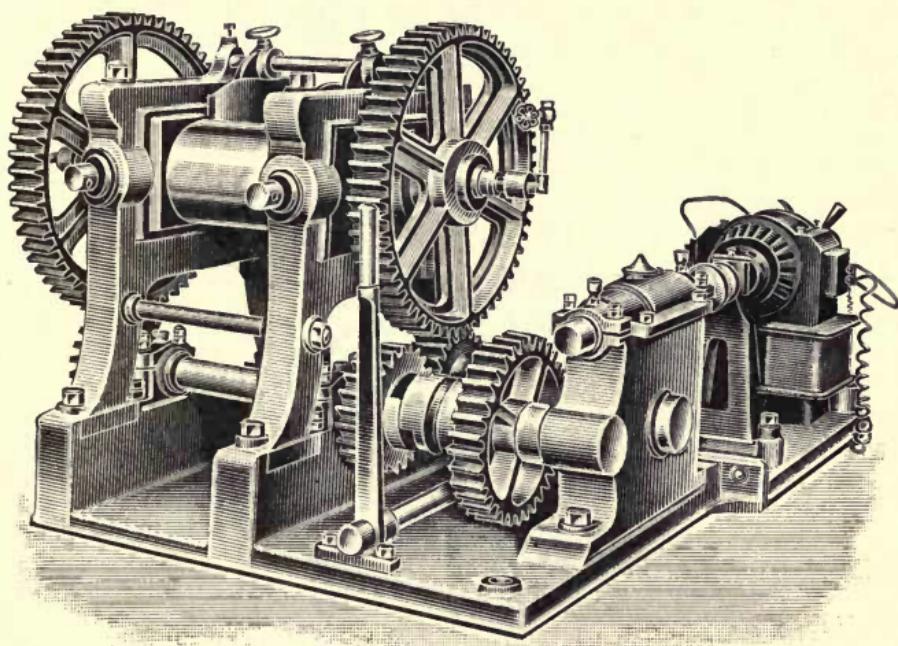


FIG. 6 (Scale 1:20).

similar mill,² having rollers 9 in. by $4\frac{1}{2}$ in. and a friction-clutch for belt drive, is shown in Fig. 7. Another laboratory mill,³ characterized by slighter build and more elongated rollers, viz., $14\frac{1}{2}$ in. by $5\frac{1}{2}$ in., is shown in Fig. 8. In so far as they are used for mixing or sheeting, it should be noted that for a given size of rollers there are both an upper and a lower limit to the amount of material

¹ By Messrs. Iddon Bros., Leyland.

² By Messrs. D. Bridge & Co., Manchester.

³ By Messrs. H. Berstorff, Hanover.

with which these mills can effectively deal. Rollers of the above-mentioned order of magnitude would take a minimum batch of about 50 gr. of rubber dough and a maximum of about 500 gr.

WATER STEAM

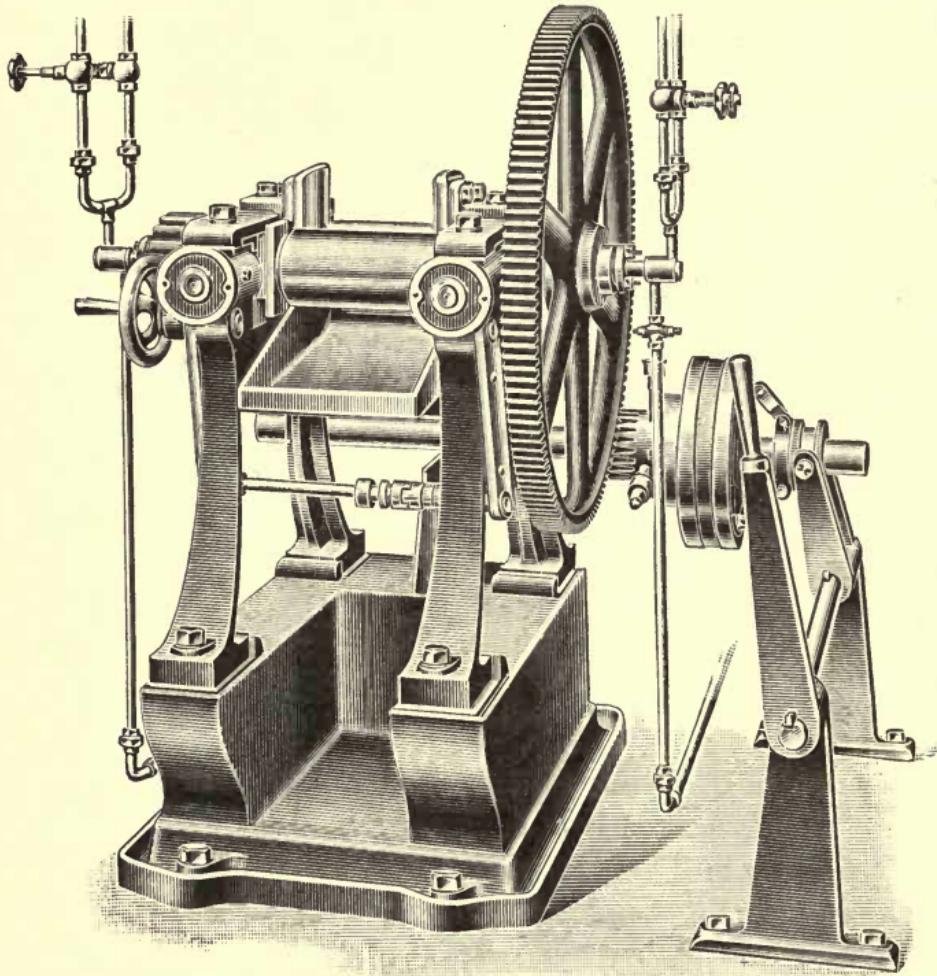


FIG. 7 (Scale 1 :16).

A relatively inexpensive hand roller mill on the very small scale, which is often useful enough as a makeshift, is the metallurgical apparatus shown in Fig. 9. Though

inconvenient by reason of the superposed position of the rollers, it serves very well for crumbing or sheeting rubber previous to analysis, but for little else. The mill is made

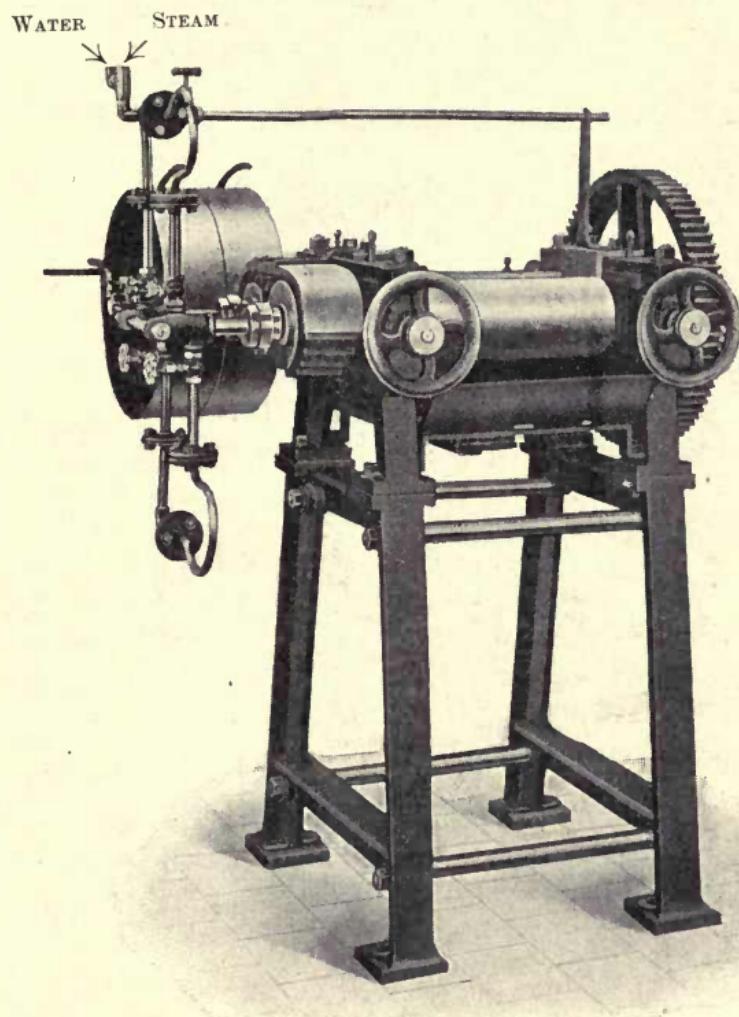


Fig. 8 (Scale 1 : 17)

in several sizes, with rollers from 2 in. by $1\frac{1}{2}$ in. to 4 in. by $2\frac{1}{4}$ in.

Centrifugal Machinery.—A laboratory in which much

general rubber work is done can ill dispense with a centrifugal machine or "centrifuge." This piece of apparatus is a necessity in certain phases of rubber

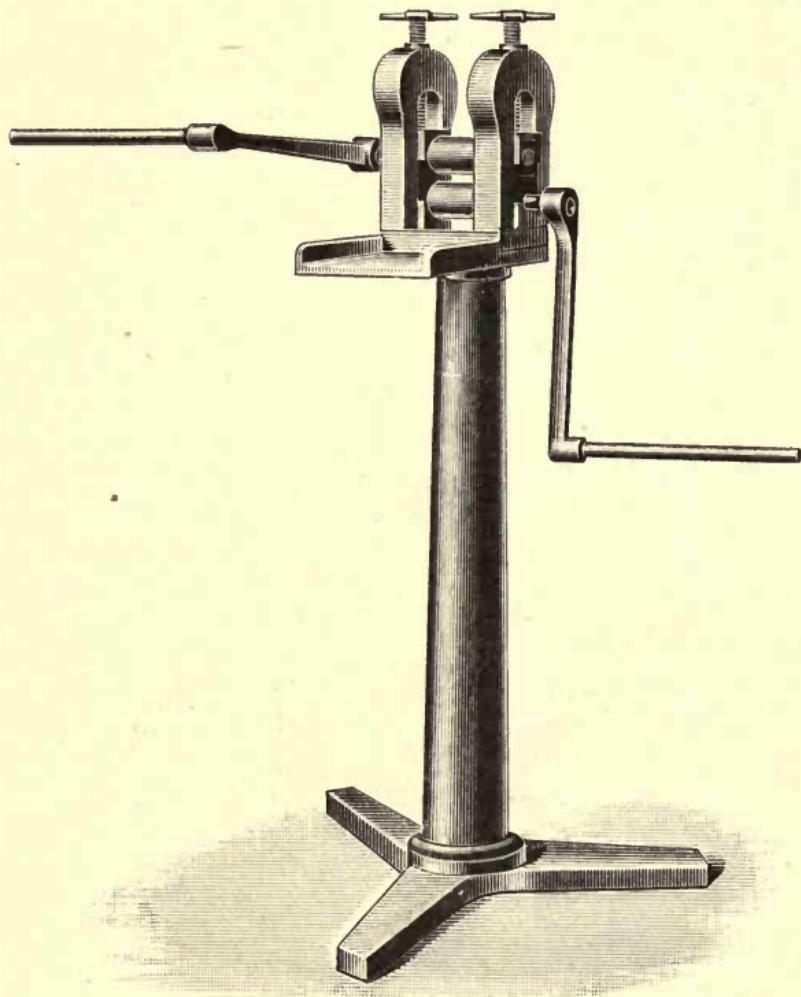
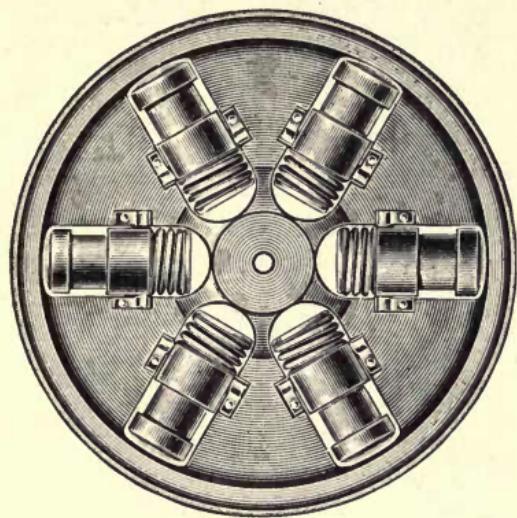
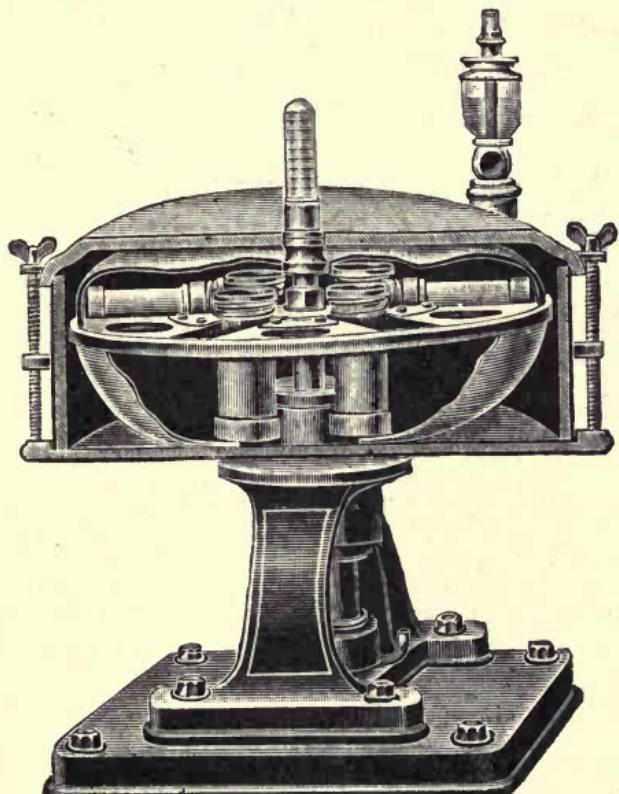


FIG. 9 (Scale 1 :14).

analysis and is in general extremely useful in all sorts of cases where solid matter in liquid suspension resists filtration or does not readily settle. The centrifuge should be of tolerable size, say of 18—20 cm. whirling



PLAN.



ELEVATION.

FIG. 10 (Scale 1 : 8)

radius, and should be driven at 1,500—2,000 revolutions per minute. The most convenient drive is from an electric motor of $\frac{1}{2}$ H.P. or so, which may either be built-on or transmit directly through a belt. A stout metal bowl enclosing the whirling parts is a *sine qua non*. There will be four, six or eight whirling-arms carrying glass vessels which should have a capacity of at least 60 c.c. apiece. A solidly-built six-armed centrifuge¹ carrying cylindrical vessels is shown on plan and elevation in Fig. 10. The machine is fitted

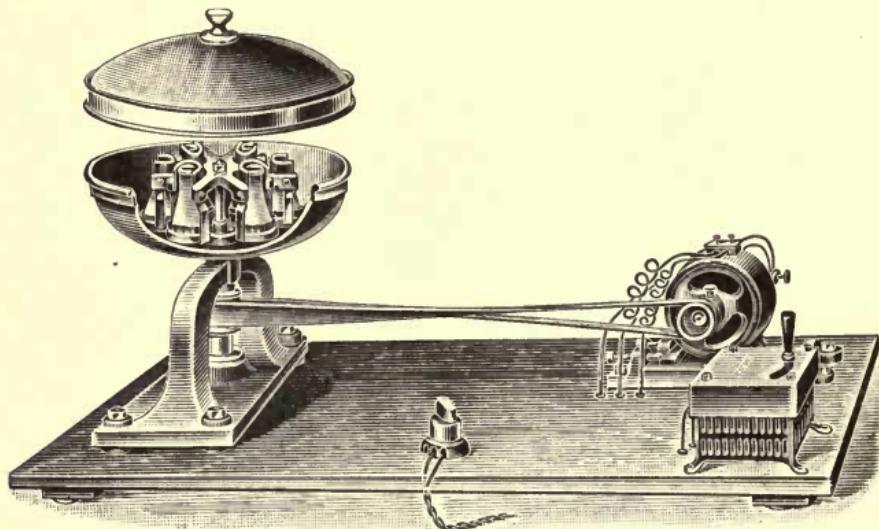


FIG. 11 (Scale 1 : 18).

with a speed-gauge, and the cylinder-holders rest upon springs intended to counteract errors of balance. Specially designed for rubber work is the six-armed centrifuge² shown in Fig. 11, which, though of slight build, does very good service. A special pear-shaped vessel (Fig. 12) is used with this machine, weighing about 40 gr. and having a capacity of about 150 c.c. The

¹ By Messrs. A. Gallenkamp & Co., London.

² By the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin.

main points to be observed in working with centrifuges are to counterpoise opposite arms with great care, to make sure of efficient lubrication, and to start the machine very gradually. A free-wheel mechanism on the spindle may be dispensed with if the drive is from an electric motor without interposed gearing.

Laboratory Apparatus.—Machinery being housed in a separate room, the rubber laboratory proper may be similar to any other laboratory in which both inorganic and organic analyses are performed. Generous draught-cupboard accommodation will be required for the various fusions and incinerations, evaporations of acid liquids, etc. The processes of distillation and of boiling under reflux condensation on water-, sand-, and oil-baths play a great part in rubber analysis, and ample provision should be made for them. A few observations on useful forms of apparatus, and especially on extractors, will not be out of place.

The continuous extraction of all sorts of materials, either with acetone or with carbon disulphide, stands perhaps foremost among rubber laboratory operations. The Soxhlet and the Knöfler (Fig. 13) forms of extractor both act on the intermittent-siphon principle; in the former, the liquid, though not actually cold, is well below boiling-point; in the latter it is surrounded by its own vapour and is therefore as hot as it can be. No form of extractor can be depended upon to do its work thoroughly in which the substance is not submitted to complete immersion in the extracting liquid. Soxhlet's extractor

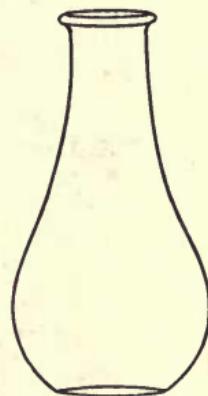


FIG. 12 (Scale 1:3).

is too well-known to need description. Knöfler's, which is the rubber extractor *par excellence*, consists of separate inner and outer tubes; to accommodate filter-thimbles of 60×25 mm., the most convenient dimensions are:—

Inner tube:—bore 28 mm., siphoning height BC 75 mm., height of wide part AC 90 mm.

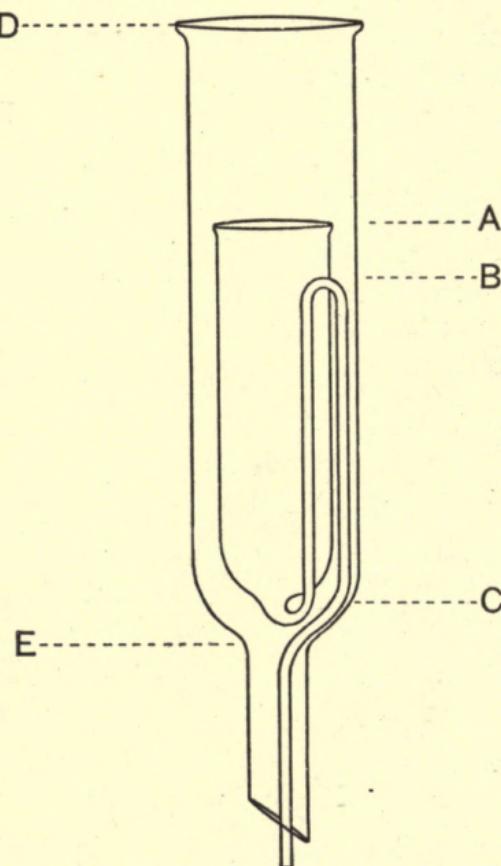


FIG. 13 (Scale 1 : 2½).

Outer tube:—bore 40 mm., height of wide part DE 150 mm.

Extractors are connected at the upper end to a reflux condenser and at the bottom to a wide-mouthed flask

(Soxhlet flask), of which the most generally convenient sizes are 100 and 150 c.c. Boiling-flasks of any other size and shape may be used, but in that case the contents should be transferred to a tared flask of the Soxhlet type before evaporating, drying, and weighing the extract. The connexions, if of cork, must be of the finest and densest material procurable. A good pair of corks which are not being used for the first time will yield about 1 mg. of dissolved solids to acetone or carbon disulphide after a ten hours' extraction. In ordinary technical rubber work an error of this magnitude is of little account, so that in general there is no harm in making use of cork connexions, provided the corks be carefully selected and subjected to preliminary extraction. Whenever it seems desirable to eliminate this source of error, recourse must be had to ground-glass connexions. This will involve not only special ground-in flasks but also special arrangements at the condenser end. The condenser may be connected up by a ground-glass joint, or else an inserted condenser may be used and such a joint rendered unnecessary. Either principle is applicable to the Soxhlet or Knöfler forms indifferently. Soxhlet's apparatus with two ground-in connexions is shown in Fig. 14. A Knöfler extractor fitted with inside condensation is seen in Fig. 15; here the elongated outer jacket serves as part of the condenser, whilst the water-cooled condenser proper (shown at the side) slides into it and rests loosely on the mouth, or may, if preferred, be fixed by a not quite air-tight cork ring, which will not come into contact with condensed solvent.

For heating the Soxhlet flask a water-bath is not very satisfactory on account of the condensed steam drippings and the loss in weight which the flask may suffer during

lengthy extractions. An excellent, but costly, mode of heating is by means of electric incandescent lamps. On general grounds, a much simpler device, viz. a talc-bath, may be recommended. This consists of a hemispherical iron sand-bath, about 10 cm. across, charged not with sand but with talc (French chalk) and heated by an

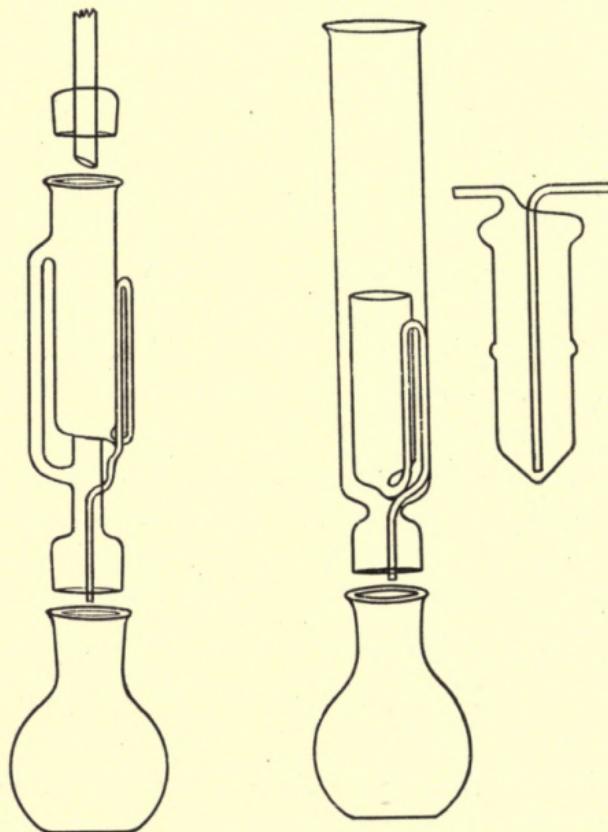


FIG. 14 (Scale 1 : 5).

FIG. 15 (Scale 1 : 5).

ordinary Bunsen burner. Little heat is wasted, the flasks are not scratched or chemically attacked, and if a crack occurs the talc forms a kind of lute and prevents a rapid outflow of solvent. In a busy laboratory an ample number of condensers and heating-baths should be permanently set up, preferably in a row against a wall,

and a sufficiency of Soxhlet flasks should be kept in stock, each of which is etched with a number and has its approximate tare recorded on a tablet hung near the balance.

Scarcely less important than acetone extraction is the boiling of substances with alcoholic alkali under reflux condensation. Cork connexions are inadmissible for this operation if there is any chance of the cork being reached by alkaline spray. A Soxhlet flask with ground-in condenser, like the gutta-percha extractor illustrated in Chap. IX., Fig. 22*b*, is a very suitable form of apparatus.

The indispensable muffle-furnace, in which incinerations are performed and batches of crucibles ignited, should be of a type which admits a fairly generous air-draught into the muffle proper. The smallest practicable size of muffle has an internal floor-area of about 6×4 in., but in general a somewhat larger area will be found more convenient. Incineration-dishes and small porcelain crucibles for igniting barium sulphate should be marked with numbers or letters and listed with their tare weights. For igniting crucibles at specially high temperatures, small one-crucible furnaces, consisting of double fire-clay cones which are slipped over a roaring Bunsen burner, are now reasonably cheap and do the work better than the laborious blowpipe.

A short tube-furnace carrying a hard glass, porcelain, or silica tube of about 12 ins. total and 6 ins. effective length is a very useful laboratory adjunct for a variety of purposes. Fig. 16 shows such a furnace constructed entirely of fireclay and heated by five gas-burners. The tube should be covered with asbestos to avoid direct impact of the flames. Electrically heated tube-furnaces

are pleasanter to work with but are much more expensive and take longer to heat up and cool down.

In conclusion, it may be mentioned that weighing to four places of decimals is usually a waste of time in a rubber laboratory. Upon one gramme weighed out, a milligramme error corresponds to an accuracy of 0·1 per cent., and on the organic side no analytical method in

rubber work can boast a greater inherent precision than this, to say nothing of the variability of samples. In inorganic determinations it may exceptionally be necessary to weigh to four places when small quantities of substance are in question.

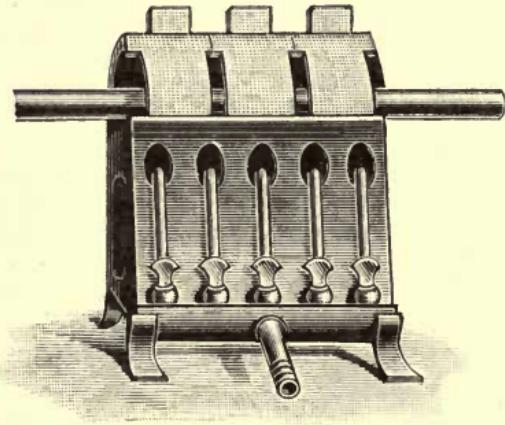


FIG. 16 (Scale 1 : 6).

At any rate, one should make perfectly sure of the third place of decimals, and this certainty is best attained by making use of a balance of the ordinary analytical type capable of weighing to four places, without troubling to adjust the tenths of a milligramme. Rubber and other bulky solids should be weighed out on a metal (aluminium or nickel) scoop provided with a counterpoise.

CHAPTER III

RUBBER DILUENTS

IF it had never occurred to anyone to mix extraneous substances (quite apart from sulphur, the vulcanizing agent) with rubber, it is safe to say that the rubber industry as we know it would be inconceivable: rubber manufacture would have expanded perhaps in volume, but hardly in scope, beyond its boundaries of pre-vulcanization times. In unvulcanized rubber we have one material, in soft-cured rubber a second, and in ebonite a third; but by admitting compounding ingredients we gain innumerable new materials. Moreover, the lowering of prices thus achieved has done much to widen the market for rubber goods. Nowadays manufactured rubber, taken in the lump, contains at least as much non-rubber as rubber.

Anything which is oily, waxy, or resinous, any homogeneous semi-solid or plastic mass free from water, or any finely-divided powder can be incorporated with raw rubber to form a smoothly uniform dough. The process by which the great bulk of soft rubber articles is manufactured consists in preparing a *dough* (by the aid of hot rollers) of rubber, sulphur, and the requisite—

pulverulent and other—compounding materials, and “curing” or “vulcanizing” this dough at temperatures of 125° — 170° for periods rarely exceeding three hours. The proper compounding materials are selected with several aims in view, e.g.:—

1. Imparting the desired physical properties, such as hardness or softness, stiffness or pliability, smoothness, strength, extensibility, and so forth; further, dielectric and insulatory properties, or resistance to chemical attack.
2. Imparting the desired colour.
3. Weighting or lightening the product as required.
4. Modifying the first cost of the product.
5. Accelerating or retarding the duration of the cure.

Technical and economic evolution has provided the manufacturer with a fairly well defined repertory of substances suitable for compounding, many of which find little or no use outside of the rubber industry. These substances fall into two main groups:—*diluents* and *pulverulent solids*.

Diluents, as the name implies, are coherent bodies, plastic, liquid, or semi-solid, which, as distinct from discontinuous solids, serve to dilute the rubber proper: they assist the rubber in its functions as a vehicle for the pulverulent *charge* which it has to carry. In the nature of things, diluents belong to the domain of organic chemistry, whilst the materials constituting charge are with few exceptions inorganic. The diluents in common use are factice, reclaimed rubber, pitches, waxes, oils, and resins. They are all considerably cheaper than rubber, and those which can be incorporated in generous proportions, viz., factice, reclaim, and bitumen, are added

primarily with a view to cheapening the product. Needless to say, each diluent exercises a specific mechanical effect, both in the dough and in the finished goods, which must be duly taken into account. In the case of such diluents as waxes and oils, which are seldom introduced in proportions exceeding one-tenth of the rubber, specific effect rather than cheapness is [the dominant consideration.

Factice.

Syn. *Substitute, Vulcanized Oil* (Ger. Faktis, Oelkautschuk, Fr. Factice).—Before the advent of reclaimed rubber, this was the only rubber diluent in a large way known to commerce, nor is it at all likely to become obsolete. Factice not only has in itself something of the feel and appearance of rubber (whence the names “rubber substitute” and “Para français”), but it can be added in large proportions, even 1:1 or over, without greatly affecting the elastic properties of the rubber. This is owing to the curious mechanical consistency of factice, which possesses compressile elasticity in a high degree, though it is all but destitute of tensile strength. Hence added factice, whilst somewhat diminishing the strength of a rubber article, does not proportionately impair its springiness. Moreover, factice, of which (free from mineral oil and wax) the specific gravity varies between 0·98 and 1·02, is the only effective material with which floating rubber goods, other than black ones, can to any important extent be cheapened. White factice was discovered in the early fifties of last century, brown factice a little later; both varieties were well established as rubber diluents in the ensuing decade.

Factice is a product of the action of sulphur chloride

at moderate (80° — 100°) or of sulphur at somewhat high (160° — 200°) temperatures upon raw or blown glyceride oils. In many respects its mode of formation is analogous to the vulcanization of rubber itself. What particular oil serves as raw material depends largely on market prices for the time being; the best results, however, are obtained with castor and rape oils. Sulphur chloride yields a light-coloured product known as *White Factice*, whereas factice made with sulphur alone has a dark colour and is distinctively called *Brown Factice*. The necessary proportion of sulphur or chlorine of vulcanization in factices may be brought within reasonable limits by previously blowing the oil; this is of especial importance with white factice, in which high vulcanization is inconsistent with stability, and 6—7 per cent. of sulphur is the usual thing. Brown factices, on the other hand, may contain from about 7 to about 20 per cent. of combined sulphur; the soft low-sulphur sorts can be made only from strongly blown oils and are very different in character from the stiff high-sulphur sorts, which are mostly made from raw oils.

Factices are solid bodies of the consistency of stiff jelly, insoluble in rubber solvents but swelling up in them to form very dilute gels. Whilst in general inert chemically, they are eminently saponifiable. Aqueous alkalies under drastic conditions and superheated steam decompose them slowly; alcoholic alkalies split them with great ease into glycerine and fatty acids of which the alkali salts are soluble in water. Brown factice is the kind chiefly used in heat-cured rubber mixings, white factice in cold-cured; but moderate admixtures of white factice are quite admissible in the heat-cure.

Factice contains normally (1) unvulcanized fatty oil, (2) a little free sulphur, and (3) factice proper, including

sulphur and chlorine (if any). Many brown factices also contain admixtures of paraffin wax or heavy petroleum fractions. These latter are incorporated with the oil before vulcanization, and have more than one advantage from the factice-maker's standpoint. They are not to be regarded by the rubber manufacturer as adulterations, provided he be aware of their nature and amount. Brown factice is made in compact slabs, 10—30 cm. thick, and is usually delivered in this form. White factice is sent out either in crushed amber-coloured lumps of irregular size, or ground into white powder of a fluffy or crumby consistency. It is important to note that the chemical composition of compact factice may vary widely from spot to spot. A package of slab or lump material should never be analysed on a single small fragment. A sample of at least 500 gr. should be drawn and thoroughly mixed by grinding between cold rollers. The analysis of factice is carried out as follows :—

1. *Extract.*—Two gr. of ground factice are placed in a filter-thimble plugged with fat-free cotton wool, and extracted with acetone for 10 hours in a Soxhlet or Knöfler tube. The extract is dried at 110° and weighed; it comprises unvulcanized oil, unsaponifiable matter (if any), and free sulphur. The presence of paraffin may be detected in the acetone solution by its crystallising out, that of mineral oil by its fluorescence. As for the unvulcanized glyceride oil, it is but sparingly soluble in acetone and is often seen to settle out in heavy drops. This substance is not really unchanged fatty oil, but always contains one or two per cent. of combined sulphur. Nevertheless, it is an oil, as distinct from a gelatinous solid, and therefore "unvulcanized oil" is not a misnomer.

2. For the determination of *free sulphur* the three

methods given in Chapter VII (p. 116) for the case of vulcanized rubber are available. The most expeditious method consists in exhausting the acetone extract with petroleum spirit saturated with sulphur, but it should be resorted to only in presence of a fair amount of sulphur, *e.g.*, when sulphur crystals are plainly visible. The method of Davis and Foucar gives trustworthy results with large or small amounts of sulphur but breaks down in presence of chlorine and is therefore out of court for white factice. The oxidation method has the disadvantage that the small proportion of combined sulphur existing in factice-extracts undergoes partial oxidation, thus increasing the apparent free sulphur. In brown factice there is seldom more than 1 per cent. of free sulphur, and mostly considerably less. Whenever the amount of free sulphur is large, faulty manufacture is indicated. White factice usually contains one or two, and sometimes several, per cent. of free sulphur, which is always produced to some extent in the reaction between sulphur chloride and oil; its presence may also be due in part to "reversion" of the manufactured factice.

3. *Unsaponifiable Matter* (*i.e.* hydrocarbons) is determined in the acetone extract from a separate 2 gr. lot of factice. This extract is boiled for two hours with 40 c.c. of *N/1* alcoholic potash. The further procedure depends upon whether the unsaponifiable is solid (paraffin, ceresine) or liquid (mineral oil, vaseline), which is easily ascertained by cooling or watering a portion of the alcoholic solution. If it is liquid, the alcohol is distilled off, the residue is taken up with water and shaken with two or three batches of ether, and the ethereal extract is evaporated, dried at 110°, and weighed. Should the unsaponifiable be solid, it will be necessary to extract with petroleum

ether (B. P. 40°—60°); in this case the alcoholic liquid is not evaporated but diluted with an equal volume of water and then shaken up with solvent. Aqueous or weakly alcoholic alkaline solutions cannot readily be extracted with petroleum ether owing to the formation of persistent emulsions.¹ The petroleum ether solution is separated and washed, first with a few c.c. of concentrated sulphuric acid, then with semi-alcoholic caustic potash solution; it is finally evaporated and dried as usual.

4. Free sulphur and unsaponifiable subtracted from total acetone extract give *unvulcanized oil*. The residue insoluble in acetone represents vulcanized oil or *factice proper*. In order to determine *combined sulphur* and *chlorine*, $\frac{1}{2}$ gr. (brown factice) or 1 gr. (white factice) of this residue is treated by the nitrate fusion (see p. 128) or potash-peroxide method. The latter is carried out thus :—

The substance is gently heated in an iron bowl (*cf.* p. 129) with 10 gr. of stick-potash and 10 c.c. of alcohol. Factice goes into solution, whilst the solvent slowly evaporates. One c.c. of water is added and heat is more vigorously applied, the bowl being frequently stirred or shaken. The bulk of the organic matter is allowed to fume off until the contents of the bowl form a thick, partially charred magma which shows a tendency to incandesce here and there. Sodium peroxide is now cautiously sprinkled in from a spatula, with continual agitation. As more and more peroxide is added, the melt becomes more fluid and finally darkens owing to formation of ferrates. Care must be taken that every part of the bowl receives its share of peroxide, so that the whole contents are uniformly oxidized. The melt is then cooled

¹ M. Hönig and G. Spitz, *Z. Angew. Chem.*, 4 (1891), p. 565.

and taken up with water. If chlorine is absent, the solution is acidified with hydrochloric acid, boiled up, and precipitated with barium chloride. In presence of chlorine, the solution is halved, and chlorine and sulphur are determined in the moieties acidified with nitric and hydrochloric acid respectively.

Alternatively, *total sulphur* may be determined, by the above or other method, in the original factice. Provided that one or the other practice be adhered to, it is mainly a matter of taste whether original or acetone-extracted material be taken. In the latter case combined sulphur (as a percentage of original factice) always comes out slightly lower, at any rate in brown factices.

5. *Moisture* is seldom worth determining in brown factice. White factice which is well advanced in decomposition may contain several per cent. Moisture is best determined by drying at 60°.

6. *Free Acid*, i.e. organic acid, is always present, generally in quantities not exceeding 2 per cent. calculated as oleic. It is quite harmless, or rather not less so than unvulcanized oil. Free sulphuric acid may occur in decomposed factice; it is detected and determined by shaking the ground material with hot water, filtering clear, and boiling with barium chloride.

7. *Ash* in brown factice is mostly well under 1 per cent. and has no particular significance. White factice often receives an addition, in the manufacture, of a few per cent. of lime or magnesia intended to neutralize any hydrochloric acid which may be split off. The ash of white factice should be not only determined but examined qualitatively.

Some recent analyses of factice, in which all the percentages are calculated upon original substances :—

WHITE.

	English.	German.	French.
Unvulc. Oil	10·3	7·7	13·8
Free Sulphur	0·8	0·3	2·1
Vulc. Oil (by difference)	86·2	89·4	81·3
Combined Sulphur (in extracted factice)	6·7	7·2	6·4
Chlorine	7·8	7·7	7·2
Ash	1·0	2·6	2·8

BROWN, FREE FROM HYDROCARBONS.

	English, hard.	German, soft.	German, medium.	German, hard.	French, medium.
Unvulc. Oil	21·7	22·7	17·2	9·6	23·6
Free Sulphur	0·3	0·2	0·1	0·1	1·5
Vulc. Oil (by difference)	77·1	77·0	82·5	90·2	74·3
Combined Sulphur (in extracted factice) . .	13·1	7·1	10·2	16·3	9·8
Ash	0·9	0·1	0·1	0·1	0·6

BROWN, CONTAINING HYDROCARBONS.

	English.	German I.	German II (Para français).	French (Para français).
Unvulc. Oil	25·1	10·6	25·0	23·4
Free Sulphur	2·5	1·6	0·5	0·4
Paraffin Wax	20·1	—	21·3	25·2
Mineral Oil	—	23·1	—	—
Vulc. Oil (by difference) . .	51·3	64·6	52·5	47·9
Combined Sulphur (in ex- tracted factice)	13·8	13·5	3·6	3·1
Ash	0·1	0·1	0·7	0·1

Other things being equal, the less unvulcanized oil there is in a factice, the better. This constituent has the

same effect in a rubber mixing as glyceride oil pure and simple, which is credited with a tendency to shorten the life of the goods. Mineral oil is less open to this objection, and paraffin not at all. In compounding a rubber with factice containing either of these constituents, their specific effects must be taken into account; for instance, when 30 parts of the favourite "Para français" type of factice are added to 100 of rubber, there will be 8-9 parts of paraffin present, which verges upon high proportions. The ash of white factice should not overstep reasonable limits, say four per cent., and should be magnesian rather than calcareous: magnesia with insufficient hydrochloric acid forms a non-deliquescent oxychloride, which lime does not, and the presence of hygroscopic matter induces slow decomposition in white factice on storage. On the whole, the best white factices are those which, in the ground state, are the driest and least coherent. Sulphur and chlorine together should not exceed 20 per cent.

Brown factice, unlike white, offers a considerable range of mechanical consistencies depending, when allowance is made for the specific influences exercised by unvulcanized and unsaponifiable, mainly on the amount of combined sulphur. At the low-vulcanization end of the series we have soft, sticky, gelatinous products; at the opposite end stiff, crisp, caseous ones. These properties are, naturally, of high importance in the choice of a suitable factice for a given mixing.

Running deliveries of factice should be assayed for acetone extract, free sulphur, and (if present) unsaponifiable. For one and the same brand they should not vary seriously in consistency and the percentage of extract should remain fairly constant, say within 2 per cent. above or below the mean. Except in a rough way, the

mechanical properties of factices of different makes cannot fairly be judged by analytical data alone. Thus two specimens made from different or unequally blown oils may show identical contents of acetone extract and combined sulphur and yet behave very dissimilarly. In such cases experimental mixings and vulcanizations must decide. A knowledge of the free sulphur content is of value chiefly with respect to compounding-calculations; an inordinate amount, however, e.g. more than 3 per cent., may indicate faulty manufacture or "reversion" in storage.

Little or nothing is to be gained by applying the standard methods of fat-analysis to factice. Information thus supposed to be obtained as to the raw material of manufacture is largely illusory and in any case is of little interest to the rubber manufacturer. The saponification numbers of factices are much higher than those of oils, and are constant only when saponification is carried out by a strictly uniform method; they mostly lie in the neighbourhood of 300 for white factice and between 180 and 250 for brown. The *yield of fatty acids* from factice is a datum which plays some part in general rubber analysis (see p. 124).

Rubber Waste and Reclaim.

For many decades past it has been the practice in rubber works to use up vulcanized waste by grinding it to powder on cold rollers and incorporating it with fresh rubber for the manufacture of goods of inferior quality. As time went on, chemical processes for removing tissue &c. from the waste were devised, and it was further found that a modest degree of plasticity could be imparted to some kinds of waste by treatment with oils. Rubber waste,

however, remains rubber waste. It can only be used in conjunction with fresh rubber and always imparts a certain lack of homogeneity to the resulting product. It still plays its part inside factories, but is seldom nowadays bought from outside as a compounding material.

Quite another thing is *reclaimed rubber*, which is now bought and sold in enormous quantities. It is prepared from ground waste by treatment with water at high temperatures (in the neighbourhood of 180°) in presence of acid or, more usually, of caustic alkali. The material is thereby rendered plastic, so that it can be sheeted like unvulcanized dough; though containing the original combined sulphur intact, it can be revulcanized with added sulphur like virgin rubber. Reclaimed rubber is of utility chiefly as a cheapening agent in admixture with fresh rubber; to considerable extent also, inferior rubber goods are now made from reclaimed rubber alone, plus filling materials.

Reclaimed rubber, or *reclaim* for short (Ger. Regenerat, Fr. Régénéré), comes into trade in compact sheets 5 to 25 cm. thick, less often in tight rolls of very thin sheet, and has the appearance and feel of stiff half-cured dough. Black, red, white, and grey sorts are current. As may be imagined, reclaim is an exceedingly variable substance, a wide range (especially as regards content of mineral matter) being procurable in each colour.

The suitability of a reclaim for use in manufacture may best be decided upon by a combination of vulcanization experiments and chemical tests. From the analytical data alone, however, a shrewd technologist will often derive all the information he needs. Chemical examination of current deliveries, to secure uniformity, is of especial

importance with reclaim. The complete analysis is identical with that of a complicated manufactured rubber (see Chaps. VII and VIII) and is seldom worth carrying out. As a rule, the following determinations are sufficient:—

1. *Specific Gravity*.—A compact piece of 5–10 gr. weight is cut off and weighed in air and water (see p. 105). The specific gravity of a reclaim must be known in order to calculate that of mixings in which it is included.

2. *Acetone Extract*.—Two gr. of reclaim, crumbed or cut up fine, are extracted for ten hours in a Knöfler tube, and the extract is dried for 3 hours at 110° and weighed. Acetone extracts usually run high, containing, as they do, the mineral, fatty, or rosin oil which is almost invariably added to reclaims to enhance their plasticity. Free sulphur rarely occurs except in red reclaims: in the reclaiming process red rubber turns grey and is restored to colour by the addition of antimony red, whereby a little free sulphur is imported.

3. *Factice*.—The acetone-extracted substance is dried, turned into a small flask with ground-glass connexions, and boiled for three hours under reflux with 50 c.c. of N/5 alcoholic potash solution. The extract is freed from alcohol and the residual reclaim is boiled out with water. The combined aqueous extract is acidified and shaken with ether, the ethereal solution being evaporated, dried, and weighed (*cf.* p. 124). By multiplying the result by 1·1 the weight of factice proper is found. In order that the extraction of factice may be complete, it is essential that the reclaim be as finely divided as possible. Few reclaims, even among those manufactured by the alkali process, fail to show one or two per cent. of matter insoluble in acetone but soluble in alcoholic potash, which

may or may not consist of real factice. The deliberate incorporation of factice in reclaim is not an unknown practice.

4. *Ash.*—Two gr. are incinerated in the usual way. It is approximately correct to regard ash as equivalent to the mineral matter present, though it mostly falls a little short of the latter.

The percentages of extract plus factice plus ash subtracted from 100 give roughly the percentage of rubber, and this is the figure of merit by which the value of a reclaim may best be judged. As a further empirical test of quality, the consistency of the reclaim after acetone extraction should be noted: the softer and stickier it is, the more likely it is to mix well and yield rubber-like products. Black reclaims of sp. gr. up to 1·1 are richest in rubber (70—80 per cent.), but there are plenty of blacks of higher sp. gr. with correspondingly smaller rubber contents. Floating blacks sometimes contain a great deal (up to 30 per cent.) of factice. The carbon black occurring in many black reclaims will masquerade as rubber unless specially determined by the method on p. 155, but the amount is usually trifling. Red reclaims similarly cover a wide range and may show anything from 40 to 70 per cent. of rubber. White reclaims are always heavy and full of mineral loading; the rubber content mostly lies between 30 and 50 per cent.

Acetone extracts of black reclaim generally run from 10 to 30 per cent., those of reds and whites being, as a rule, rather lower. Part of this extract is always added oil, which, in addition to its plasticizing action, has the desirable effect of restraining the tendency to extremely rapid vulcanization which is characteristic of reclaimed rubber.

Reclaims intended to be used for thin sheet goods must contain the very minimum of mineral or metallic grit, and in this case it is well to dissolve a gramme or two as on p. 141 and submit the separated pulverulent matter to minute inspection. Few reclaims, as is only natural, are wholly free from coarse solid particles.

In a small way, reclaims made from unvulcanized waste and intended for making rubber solutions are put on the market. These should be examined by treatment with 100 parts of benzene or solvent naphtha. Undissolved gelatinous particles which are retained by a sieve point to the presence of vulcanized rubber.

Bitumens and Pitches.

Natural bitumen, especially Trinidad and Syrian asphaltum, has long been in use as a compounding material, notably in cable-coverings, to which it is added in order to diminish micro-porosity and increase the insulation. It is only within the last few years, however, that bitumen, in the form of *Mineral Rubber* so-called, has come into any great vogue as a filler for rubber goods generally. Mineral Rubber is essentially a diluent and a cheapener, like factice; it mixes readily with rubber and can quite well be added to the extent of 50 per cent. of the rubber or even more. It is a tough black non-fluid substance yielding to pressure but capable of breaking with vitreous fracture, and is prepared either from soft natural bitumens or from blown petroleum residues, or from mixtures of both. There is little, if any, chemical difference between the essential constituents of the one and the other, and the distinction is of small moment from the rubber point of view. The value of a mineral rubber depends on its behaviour when

incorporated in the mixing and vulcanized, which, in the present state of knowledge, there is no certain means of judging except by direct experiment. As a rough guide, it may be said that bitumens of high softening-point produce strong rubbers with a tendency to defective resiliency, whilst low softening-points correspond to poor tensile strength but comparatively good resiliency. Provided that a mineral rubber be an asphaltum or petroleum product containing little or no ash, and that it be free from water, mineral acid, and admixtures of coal-, wood-, or stearine-pitch, the minuter questions of its applicability must be settled by making experimental mixings. Laboratory tests are useful mainly for controlling uniformity in running deliveries.

1. *Asphaltene Content, &c.*—One gr. of substance is treated in the cold with 50 c.c. of light petroleum spirit. After soaking for some hours, the softened bitumen is crushed with a glass rod or in a mortar and well shaken up with the liquid. The thoroughly settled solution is filtered, and the black pulverulent residue is washed by decantation and on the filter with petroleum spirit. The brown *petrolene* fraction now in solution is of a greasy or treacly consistency and often contains appreciable quantities of paraffin wax. The residue on the filter is dissolved in benzene or carbon disulphide, when mineral matter and pulverulent carbon, if present, remain on the filter and may be weighed; the clear solution is evaporated in a tared flask, dried at 110°, and weighed. *Asphaltene* thus isolated is a shiny black brittle substance which does not soften until temperatures well above 150° are reached. Mineral rubbers usually contain about 30 per cent. of asphaltene. Carbon, if present in any considerable amount, points to an admixture of coal-tar

pitch. This latter is also indicated by strongly fluorescent petroleum spirit solutions, since bituminous petrolenes have but a feeble fluorescence.

2. *Moisture*.—A qualitative test may be made by dissolving 5 gr. of substance in 100 c.c. of benzene which has been rendered anhydrous by means of sodium or by distilling off the first runnings. The solution is distilled through a dry condenser; if a marked turbidity be observed in the first drops of distillate, the sample must be regarded as objectionably moist.

3. *Softening-Point*.—This is a property which can be defined only on somewhat arbitrary and conventional lines. Softening-points, to be comparable, must be determined by a strictly uniform method. That of G. Krämer and C. Sarnow¹ (modified by L. Barta²), which is much in use for asphalts, may be carried out as follows:—

Pieces of glass tube of 6 mm. bore are cut and ground true at the ends so as to be exactly 5 cm. long. Such a tube is filled with melted and well stirred bitumen by pouring or by suction, care being taken to avoid enclosures of air. After cooling, the surplus of bitumen is shaved off flush with the ends of the tube. The filled tube is connected by means of rubber—glass to glass—with a similar but longer empty tube, and exactly 5 gr. or 0·37 c.c. of mercury are poured in; the whole is then fixed in a wide test-tube acting as air-bath, which itself stands in a bath of molten paraffin. Heat is applied at the rate of 2° per minute, and the temperature at which the mercury forces its way through the bitumen and sinks to the bottom of the test-tube is taken as the softening-point. The thermometer should stand in the air-bath, close to

¹ *Chem. Ind.*, 26, (1903), p. 55.

² *Petroleum*, 7, (1911), p. 158.

the bitumen tube. Tested by this method, mineral rubbers show softening-points ranging from 100° to 150°.

When bitumen is compounded with rubber and sulphur, and vulcanized, it undergoes chemical changes, part of it combining with sulphur and becoming insoluble in rubber solvents, like the vulcanized rubber itself. The subjoined experimental results give some idea of the behaviour of bitumen towards solvents after vulcanization, which is of especial interest with regard to the analysis of rubber goods. The bitumen used for these experiments was one of the best known brands of the "mineral rubber" class. Each mixing was vulcanized at 138° for varying periods and then analysed in the usual way. The figures, all but the last row, stand for percentages upon original material.

From the figures on p. 55 it will be seen that the bitumen has undergone partition, in round numbers, as follows:—

	A.	B.	C.
Acetone-Soluble	58	70	76
Soluble in Carbon Disulphide	17	14	14
Insoluble	25	16	10
	100	100	100

It will further be perceived that the degrees of sulphur (coefficients of vulcanization, *cf.* p. 126), which in the present cases are referred not to pure rubber but to a mixture of rubber and insoluble bitumen, come out abnormally high, especially when a large proportion of bitumen has been added to the mixing. That is, bitumen, no less than rubber, is a vulcanizable material. Both from the manufacturing and the analytical points of view, then, one has

A. Para 100, Bitumen 50, Sulphur 10 (Bitumen = 31.2 per cent.).
 B. Para 100, Bitumen 20, Sulphur 10 (Bitumen = 15.4 per cent.).
 C. Para 100, Bitumen 5, Sulphur 10 (Bitumen = 4.35 per cent.).

	A.			B.			C.		
	2 h.	2½ h.	3 h.	2 h.	2½ h.	3 h.	2 h.	2½ h.	3 h.
Acetone Extract	24.0	23.3	22.4	18.7	17.8	17.0	12.8	12.1	11.6
Rubber-Resin (separately determined)	2.4	2.4	2.4	2.9	2.9	2.9	3.3	3.3	3.3
Free Sulphur	3.3	2.7	2.0	4.9	4.2	3.7	6.1	5.5	5.0
Bitumen soluble in Acetone (by difference)	18.3	18.2	18.0	10.9	10.7	10.5	3.4	3.3	3.3
Carbon Disulphide Extract . . .	5.6	5.4	5.3	2.4	2.2	2.1	0.7	0.6	0.5
Total Bitumen extracted . . .	23.9	23.6	23.3	13.3	12.9	12.6	4.1	3.9	3.8
Residual Bitumen (by difference)	7.3	7.6	7.9	2.1	2.5	2.8	0.25	0.45	0.55
Combined Sulphur	2.78	3.28	3.88	2.78	3.22	3.78	2.49	3.09	3.62
Coefficient of Vulcanization . .	4.10	4.82	5.67	3.66	4.18	4.95	2.97	3.67	4.35

to reckon with the absorption of sulphur by bitumen and the partial production of a new substance, insoluble in carbon disulphide and containing combined sulphur, distinct from the original bitumen.

Coal-Tar Pitch is an old-established ingredient of inferior black mixings, in which it acts more or less as a substitute for bitumen. The association of coal-tar pitch with overshoe rubbers, especially, has become almost classical. Coal-tar pitch cannot be added to rubber in any very large proportion owing to its odour and its content of finely-divided carbon. This carbon is characteristic of coal-tar pitch and is usually present to the extent of about 30 per cent., but as much as 40 per cent. is not uncommon. To determine carbon, 1 gr. of pitch is dissolved in 200 c.c. of boiling benzene, and the supernatant solution, after settling, is poured through a tared Gooch crucible. The residue is boiled up with fresh benzene at least twice. Finally, the residue is rinsed into the filter, washed, dried, and weighed. Coal-tar pitch should contain less than 1 per cent. of mineral matter. Softening-points are determined as in the case of bitumen.

Resins.

Since all rubbers are themselves more or less resinous, it would seem a very natural thing to dilute rubber with added resin. Apart from the fact, however, that there is no great profusion of suitable resins available, admixtures of resin are relatively far more detrimental to the valuable mechanical properties and durability of vulcanized rubber than admixtures of factice or bitumen. One advantage which resin undoubtedly possesses is that it does not interfere with the pigmentation of the mixing. Ordinary *Rosin* (colophony) is used

to some small extent in soft rubbers. The comparatively high-priced hard resins, *Shellac*, *Copal*, *Acroides*, *Sandarac*, *Dammar*, etc., find a limited application as compounding materials for ebonite (*cf.* p. 137). In place of resin proper, it is a very common practice to make use of the various rubber-containing resins treated of in the following section.

Rubber-Containing Resins.—The gums classifiable as rubber can be arranged in order of their resin-content until a lower limit of about two parts of true rubber to one of resin is reached. Nature then leaves a gap, and the series recommences with gums in which resin is the principal constituent, at a ratio of about one of rubber to two of resin. Rubber-containing resins of this sort are produced in tolerably large quantities in Borneo, Sumatra, and the Malay Peninsula, and are employed not only in vulcanized and unvulcanized rubber compositions, but also extensively outside the rubber industry, *e.g.*, for cements, chewing-gum, etc. West Africa, also, exports so-called flake and paste rubbers which belong essentially to this category. The Asiatic sorts are known by a variety of names, *Jelutong*, *Palembang*, *Besk*, *Pontianak*, *Dead Borneo*, etc. Qualitatively these gums are much alike; moreover, their nomenclature is by no means sharply defined. In the raw state they contain widely-fluctuating amounts of moisture, according to the degree to which they have been dried naturally or artificially: fresh *Jelutong* may be more than half water, and has the appearance of cream cheese. Mechanical impurities are mostly low in amount. The ratio of rubber to resin, again, is subject to variation; on the average it runs about 1:3. *Jelutong* occasionally shows 1:2, whilst at the other end *Dead Borneo* shows ratios more like 1:5 or

1:6. The subjoined analyses, without pretending to represent types or averages, may be cited by way of example :—

	Jelutong I.	Jelutong II.	Pontianak.	Dead Borneo.
Moisture	52·5	16·5	2·7	19·1
Dirt	1·0	0·8	0·4	1·6
Resin	35·1	65·6	72·7	68·2
Rubber (by difference)	11·4	17·1	24·2	11·1
	100·0	100·0	100·0	100·0

The pure resins isolated from these gums are hard and subcrystalline, and are thus very different from the resins accompanying ordinary rubber. The rubber-like hydrocarbons contained in them are usually weak and soft. The gums themselves possess, or should possess if not too much oxidized, a peculiar tackiness and ropiness which are not the least valuable of their properties. Rubber-containing resins are not to be confused with low-grade gutta-perchas containing resin and hydrocarbon in similar proportions, some of which are of a moist, caseous, Jelutong-like consistency. After removal of the resin by solvents, there is no difficulty in deciding whether the residual hydrocarbon is rubber or gutta-percha.

The analytical data to be determined are moisture, resin, and dirt, rubber being estimated by difference. From large lots, samples are best taken after the material has been washed, or at least sheeted, and dried. When a hand-sample is analysed, moisture is first determined on a carefully-averaged portion of about 50 gr., or still better on the whole sample, and the further determinations are carried out on portions of the dried mass. Moisture

is determined as usual by heating to constancy at 95° in the vacuum-oven or at 110° in a current of indifferent gas. Accuracy in moisture determinations is of importance, because the percentage of rubber, which is itself small, is arrived at by difference; for this reason, also, the determination of moisture in technically dried material should never be omitted.

Resin and dirt are best determined after dehydration, but no great harm is done by taking original material if it contains only a few per cent. of moisture. Resin is determined by extracting 1—2 gr. in a Soxhlet tube with acetone. For this purpose the gum is preferably rolled flat on a sheet of extracted filter-paper, which is then wrapped into a spiral; or the material may be extracted in the form of snippets, the shrunken mass being eventually cut up again and re-extracted. Dirt may be determined by dissolving 2—5 gr. in benzene and filtering on to a Gooch crucible or tared filter. Rubber-containing resins also lend themselves very well to the determination of dirt by Pontio's method (see p. 172), according to which 1 gr. of substance is exposed in a tared filter to the dissolving action of toluene vapour. Mineral matter may be determined as usual by incineration.

CHAPTER IV

SOLID COMPOUNDING MATERIALS

THE general effect of pulverulent fillers in vulcanized rubber is to increase the specific gravity, tensile strength (within limits), compressile strength, and resistance to wear, and to diminish the extensibility and resiliency. In addition, each material exerts its specific effect, which may be chemical, pigmentary, or mechanical. Under the latter head the decisive factors are fineness of subdivision, as affecting the texture of the product; hardness, as affecting its resistance to attrition; and specific gravity, inasmuch as the elastic properties of a compounded rubber depend rather on the volume than on the weight of rubber present. The special uses, moreover, to which a rubber article is destined must be taken into account in the choice of filling materials (resistance to acids, alkalies, high-pressure steam; hygienic considerations, etc.). Further, all fillers (with the exception of vermillion and cadmium yellow) are in a high degree cheapening agents, and in mixings which are heavily loaded the difference in price between one filler and another is a matter of some importance. The problems which have to be faced by a technologist in making up mixings are thus exceedingly

complex, and cannot be properly solved unless he knows exactly, chemically and otherwise, what he has before him in the way of compounding materials. Conversely, the chemist who has to report on such should have sound notions on the suitability of a given material for a given mixing. A few indications in this sense have been given in the preceding chapter, and more will be given in the sequel; but this subject, besides being mainly technological, would require a treatise to itself if dealt with in detail. All this apart, the duties of a rubber laboratory are to see that the compounding materials are what they purport to be, that they are free from impurities which are noxious from the rubber-manufacturing standpoint, and that successive deliveries do not vary in such a way as to upset the manufacture. In a rubber works having its own laboratory, every consignment of compounding material should be sampled by the chemists themselves and tested, before being allowed into the mixings. This may seem a tedious and irksome proceeding, and it may well turn out that a material is reported as up to the mark hundreds of times in succession; nevertheless so many costly goods can be rendered unsaleable by a single package of untested material happening to be not up to the mark, that the rule should be adhered to inexorably.

Pulverulent compounding materials may be divided according to their function into three classes:—accelerators of vulcanization, fillers pure and simple, and pigments. There is some overlapping between these classes, and in any case all the substances in question are fillers, with or without other distinctive properties; the division, however, is a convenient one. The more important members of each class will be passed in review

below. The following general considerations on testing may be noted :—

All materials should be as finely divided as possible. Precise data as to the bearing of degree of fineness on the resulting product are as yet lacking ; but it may be taken for granted that for most goods, and certainly for thin sheet, a finer powder is preferable to a coarser. Fineness can usually be gauged with sufficient accuracy by inspection, or by rubbing between finger and thumb ; if greater accuracy be desired, experimental elutriations may be carried out. Lumps of clotted powder are undesirable, though not positively noxious ; on the other hand, coarse mechanical impurities such as fragments of wood or metal are in the highest degree objectionable. These latter cannot always be detected by means of laboratory samples, and great vigilance is therefore necessary on the part of those responsible for storing materials and weighing out mixings. The whole contents of a package in which such contaminations are known or suspected should be sent through a sieve before being put to use. With substances of a composite nature (Antimony Red, Lithopone, Black Hypo, etc.) inequality of composition within a given package is another possibility which it is well to bear in mind.

Chemical impurities which are in all cases undesirable or even fatal are moisture, free mineral acid, and copper. Pulverulent matter in equilibrium with air is seldom quite free from hygroscopic moisture and will contain more, the lighter and finer the powder ; but this generally amounts to less than 1 per cent. and may be disregarded. On the other hand, in ill-dried powders very considerable percentages of moisture are sometimes encountered. Determinations are carried out by drying from 2 to

10 gr. on a flat dish for two hours at 110°; when free sulphur is present, however, the temperature should not exceed 60°, or the drying should be done *in vacuo*. Moisture is harmful in that it is the cause of blowing and porosity during vulcanization, and is particularly dangerous when the goods are open-cured, *i.e.* not in moulds. In general, 2 per cent. may be allowed as a limit. Powders containing more than this amount of moisture should be stove-dried before being put into the mixings. All filling materials, whatever other tests be applied, should be assayed for moisture as a matter of course.

Acidity, by which is meant free sulphuric acid, is an old-established bugbear of the rubber industry, but it is lawful to believe that very often spoilt goods in which acid is found owe their acidity not to faulty raw materials but to oxidation at a later stage. Acidity need be looked for only in materials not of a decidedly basic nature, and even then will not cause trouble in mixings containing basic ingredients; in other mixings it is certainly capable of bringing about bad cures and eventual rapid decay. Free acid is easily detected and determined in aqueous extracts of the material under test (*cf.* p. 92); it is advisable not to allow more than 0·1 per cent., calculated as H_2SO_4 .

Copper, even in very small quantity, is supposed to exert a peculiar catalytic action leading to the break-down of rubber goods in the cure and after. To be on the safe side, compounding materials should be condemned when their acid solutions or extracts show a perceptible blue colour or addition of ammonia and filtration.

Accelerators.

There are three substances in common use, viz., litharge, caustic lime, and magnesia, which have the property of accelerating vulcanization, even when present to the extent of only a few per cent.; the effect is more pronounced, the greater the proportion of accelerator. This is stated to be due, at any rate as regards litharge,¹ to a heating of the dough above the actual vulcanization-temperature caused by reaction between litharge, sulphur, and rubber-resin, but the matter can hardly as yet be regarded as fully cleared up. The possibility of thus shortening the time, or lowering the temperature, of vulcanization is of incalculable technical importance: and many of the inferior rubber sorts cannot without accelerators be satisfactorily cured at all. On the other hand, the danger of over-curing has to be guarded against with especial care. Litharge is more active, but only slightly more, than lime and magnesia as an accelerator; the two latter are about equal in potency.

Litharge, PbO (Ger. Bleiglätte, Fr. Litharge), sp. gr. 9·4, is commonly supplied in a state of high chemical purity, but varies somewhat in degree of fineness and therefore in colour. It should be soluble in cold dilute nitric acid without notable effervescence or residue, and especially without leaving black flakes of the noxious lead peroxide. A little metallic lead in fine division, which is easily detected and determined with the aid of acetic or very dilute nitric acid, does no harm. The solution should show no reaction for copper.

Litharge is a decided pigment, very small admixtures of it producing a black rubber owing to formation of lead

¹ E. Seidl, *Gummi-Ztg.*, 25 (1911), pp. 710, 748.

sulphide. Very many, if not most, black and grey rubber goods are coloured by means of litharge.

White Lead, basic lead carbonate (Ger. Bleiweiss, Fr. Céruse), sp. gr. 6·1–6·2, possesses the accelerating and pigmentary properties of litharge in a reduced degree. Being in its original condition a strong white pigment, it tends to impart a bluish-grey tint to vulcanized rubber. Like all substances containing water of hydration it is liable, in unfavourable circumstances, to cause blowing. *Sublimed White Lead*, which is comin increasingly into favour, is an anhydrous basic sulphate of lead containing roughly 65–75 per cent. of PbSO_4 with 20–30 per cent. of PbO and a few per cent. of zinc oxide. It is a little denser than ordinary white lead, but serves much the same purposes. *Red Lead*, Pb_3O_4 (Ger. Mennige, Fr. Minium), sp. gr. 8·6, has a powerful accelerating action, largely due, no doubt, to the heat evolved by its reaction with sulphur; at the same time its oxidizing propensities are apt, unless kept within bounds, to extend to the rubber. It finds a limited use, chiefly in special quick-curing mixings. The cheaper kinds of red lead are subject to adulteration with white powders (calcium carbonate, barytes, &c.) and with ferric oxide. Organic dyes, which also occur as adulterants, may be detected by extraction with alcohol, dilute acid, or dilute ammonia.

Lime, $\text{Ca}(\text{OH})_2$ (Ger. Aetzkalk, Fr. Chaux), sp. gr. 2·1, is almost always nowadays used in the form of slaked lime, which is easier to store and has a finer grain than quicklime. It is added to mixings in small quantities only, and has practically no pigmentary effect. Lime should be nearly free from silica and carbonate, and should show an ignition loss corresponding within close limits to that of $\text{Ca}(\text{OH})_2$, viz. 24·3 per cent. Iron in

minute amount does no harm, but manganese, which sometimes occurs in lime, shares the evil reputation of copper and should be present in no more than traces.

Magnesia, Calcined Magnesia, MgO (Ger. Magnesia Usta, Fr. Magnésie Calcinée), sp. gr. 3·2—3·6, behaves much like lime in rubber mixings but, besides being heavier, has a rather coarser grain. It is prepared by the ignition of magnesite or artificial magnesium carbonate, and seldom consists of magnesium oxide pure and simple. Magnesias always show an ignition loss ranging from about 2 to about 20 per cent. according to the degree of calcination and of subsequent exposure to the atmosphere; hence also the bulkiness and the true density are apt to vary. Calcium and silica should not be present beyond one or two per cent., and it is well to test for manganese. When a given grade of magnesia is used for given mixings, successive deliveries should not be allowed to vary seriously in ignition loss. *Magnesium Carbonate*, which is mainly employed as an indifferent filler, has also a slight but definite accelerating effect on vulcanizations.

Fillers.

Powders coming under this heading are white, but have too little covering powder to be effective pigments. They may thus occur, even in tolerably large proportions, in red and black rubber goods. The chief members of this group are barytes, calcium and magnesium carbonates, and siliceous substances.

Barytes, BaSO₄ (Ger. Schwerspat, Fr. Baryte), sp. gr. 4·3—4·6, ranks among the most largely used materials, being a cheap, weight-giving, and perfectly indifferent body. Almost all the barytes which comes into the rubber industry consists of the mineral heavy-spar,

ground fine. It invariably contains a little fluorspar, CaF_2 ,—up to 10 per cent.—which is quite harmless except in that it reduces the specific gravity slightly. Inferior grades may further contain as impurities silica and iron; the yellow tinge imparted by the latter is sometimes cloaked by an addition of ultramarine. Barytes should be examined for its content of barium sulphate by boiling 2 gr. for half an hour with dilute hydrochloric acid, cooling, filtering, and weighing the ignited residue in a platinum crucible. A few drops of pure hydrofluoric acid are then added and fumed off, whereupon the crucible is ignited and re-weighed; the presence of any serious amount of silica is thus indicated by a loss in weight. Lead is a very undesirable impurity; in the absence of iron it may be detected by the formation of lead sulphide when a little of the powder is mixed with ammonium sulphide on a watch-glass. *Precipitated Barium Sulphate*, which is comparatively seldom employed, is finer in grain and more of a pigment. It should be examined for free acid and for calcium sulphate.

Whiting, CaCO_3 (Ger. Kreide, Fr. Blanc d'Espagne, de Meudon, &c.), sp. gr. 2·7—2·9, is another very widely used material, its chief recommendation being cheapness. It commonly consists of the mineral chalk, ground and levigated, and is sometimes far from dry. The better grades should be as free as possible from silica and iron. Manganese is not unknown as an impurity.

Silica, in the form of naturally occurring minerals (infusorial earth, kieselguhr, &c.) or of chemical precipitates, is supplied to the rubber industry in very pure white varieties, sp. gr. 1·8—2·0, largely under fancy names such as *Atmoid*. Owing to its fineness and low specific gravity it is specially useful in rubber mixings as a stiffening

agent. The analytical examination comprises moisture, ignition loss (*i.e.* water of hydration), and bases, the difference being silica. One gramme is weighed in a platinum crucible and dried at 110°; it is next ignited; finally a sufficiency of pure dilute hydrofluoric acid is added and a drop or two of sulphuric acid, the liquid is evaporated, and the residue is ignited. This residue, though consisting partially of sulphates, approximately represents the metallic oxides present; should it amount to more than 2 per cent., it is advisable to determine and deduct the combined sulphuric acid. Infusorial earth is apt to contain a good deal of moisture, anything up to 15 per cent. The ignition loss ranges from 3 to 4·5 per cent.; bases should not exceed 4 per cent. Adulterations or natural admixtures of calcium carbonate are generally apparent at first sight, and are easily dealt with analytically. *Talite* is a fine white silica, very similar to the above but denser, sp. gr. 2·2. It contains bases up to 4 per cent. and very little combined water, the ignition loss being well under 1 per cent.

Kaolin, China Clay, hydrated aluminium silicate (Ger. and Fr. *Kaolin*), sp. gr. 2·3—2·6, was formerly a very popular indifferent filler, and is still used in fairly large quantities. It should show 11—14 per cent. ignition loss, 46—48 per cent. of silica, and 38—40 per cent. of alumina, and should undergo only slight decomposition when attacked by dilute acid. *Kaolin* is apt to be very damp, moisture-contents of 20 per cent. being not unusual. *Slate Powder*, which is occasionally used as a filler, and *Ochre* (*cf.* p. 80), are also aluminosiliceous minerals, but with a fairly high content of iron.

Talc, French Chalk, hydrated magnesium silicate (Ger. *Talc*, Fr. *Talc*), sp. gr. 2·7, is an indispensable

material in rubber manufacture. Owing to its peculiar unctuousness, it finds the widest possible application for "pouncing," or dusting over, rubber surfaces intended to be non-adhesive, also moulds, boards, &c., intended to come into contact with rubber without risk of sticking. A thin film of talc will render the tackiest rubber surfaces smooth and repellent. In addition, talc is used to a considerable extent as a compounding material, to impart smoothness or stiffness, or in cable-coverings to enhance electrical insulation. Talc is graded commercially by its colour, the inferior qualities having a greyish or yellowish tone; but from the rubber point of view this matters less than the degree of unctuousness, which also is subject to slight variations. Samples for comparison may be tested by rubbing between finger and thumb. Chemically, talc shows about 6 per cent. ignition loss, 60 per cent. of silica, 9 per cent. of alumina, and 25 per cent. of magnesia; it should be quite indifferent towards moderately dilute acids. A rather common adulterant is calcium carbonate, which is easily detected and determined by the aid of dilute acid. *Mica Powder* is also sometimes used in electrotechnical rubbers, on account of its high insulating properties.

Asbestos (Ger. Asbest, Fr. Amiante), sp. gr. 2·9—3·2, is supplied both as fibre and ground into powder. In the fibrous form it is one of the most important constituents of steam-jointings and "mechanicals" generally. The special virtue of asbestos lies in the tough, felted, unyielding structure which it imparts to rubber; hence the suitability of asbestos-filled rubbers for high temperature work on the one hand, and for exerting friction, e.g. in brake-blocks, on the other. Asbestos contains water of hydration, silica, iron, and magnesia in somewhat

fluctuating proportions, and is by no means resistant, at any rate so far as concerns the magnesia, to acid attack. It does not readily lend itself to adulteration. *Pumice Powder* and *Ground Glass* are types of filling material serving special ends. The use of the former is mainly, and that of the latter wholly, confined to rubbers for abrasive purposes, e.g., pencil erasers.

Magnesium Carbonate (Ger. Kohlensaure Magnesia, Fr. Carbonate de Magnésie), sp. gr. 2·2, has of late years come into favour as a light filler. It is a bulky, fluffy powder prepared synthetically in the wet way, and is usually of high chemical purity. In composition it approximates to the formula, $MgCO_3 \cdot H_2O$. The dried powder generally shows total ignition loss 55—57 per cent., combined water 16—18 per cent., and CO_2 36—41 per cent. Combined water and CO_2 may be determined in one operation by heating 0·2 gr. of substance in a short tube-furnace, after the fashion of an organic combustion-analysis. Light magnesium carbonate differs markedly from ground magnesite, which is comparatively seldom used as a rubber material. Magnesite is much denser (sp. gr. 3·0), is free from combined water, and contains siliceous and metallic impurities.

Pigments.

It is required of rubber pigments that they shall suffer no change during vulcanization. For all the more serious classes of rubber goods, the public are accustomed to four colours only, viz., black, grey, white, and red, and expect clean and vivid tints. The palette, so to express it, of the rubber manufacturer is therefore not quite the same as that of the painter, and is practically limited to the short list of pigments reviewed below. Lead-colours, qua

pigments, are excluded, at least as regards heat-cured goods; on the other hand, antimony red is a pigment which is peculiar to the rubber industry.

The exact effect of a pigment in rubber can only be gauged by making an experimental mixing, the more so since rubbers themselves are for the most part by no means colourless. Two or more pigments of the same class may be compared by painter's test, thus:—the powders are worked into a thick paste with boiled linseed oil, deposited in lumps of equal area on glass plates, and inspected from the back, *i.e.*, through the glass. Specimens so prepared may be allowed to harden and can be preserved for reference. Pigments other than white should be diluted with a standard zinc white, blacks with 50—60 parts, other colours with two parts. Conversely, the covering power of whites may be compared by dilution with a standard lampblack. Conclusions as to the effect of pigments in vulcanized rubber from their effect in oil, must, however, be drawn with some caution.

White Pigments.

Zinc White, ZnO (Ger. Zinkweiss, Fr. Blanc de Zinc), sp. gr. 5·5—5·6, has long been and remains one of the most popular of compounding materials. Regarded merely as a pigment, it leaves something to be desired: its covering power is but moderate, and in vulcanizations conducted at medium to high vulcanization-temperatures it has a tendency to assume a yellowish tinge. The best zinc white is made from the previously isolated and purified metal and is supplied as a fine, white powder which is almost chemically pure ZnO. It should be completely soluble, without effervescence, in dilute (10 per cent.) acetic acid. This and other white pigments should

be free from iron, copper, and lead ; to test for the latter, a moderately acid solution in hydrochloric acid is treated with hydrogen sulphide, when the liquid should remain colourless. Inferior zinc whites are sometimes adulterated with barytes, whiting, kaolin, etc., and, in zinc whites intended primarily for paint-making, white lead is a possible adulterant. A defect of zinc white, not shared by zinc sulphide, is that it is liable to be leached out of rubber goods by dilute acids. For this reason zinc white is in some countries prohibited (equally with lead compounds) for articles which come into contact with foods and beverages.

Lithopone, sp. gr. 3·8—4·2, is a synthetic product obtained in the wet way by precipitating barium sulphide with zinc sulphate ; theoretically it should be a mixture of 70·5 per cent. of BaSO_4 with 29·5 per cent. of ZnS , but the conditions of manufacture admit of fluctuations. Originally a paint-making material, lithopone has become one of the most important of rubber pigments ; it possesses a high covering power and does not discolour in the cure. The valuable ingredient is the zinc sulphide, according to the content of which lithopones are commercially graded under the denomination of variously-coloured seals. The standard quality for rubber mixing is "Red Seal," which is guaranteed to contain 30 per cent. of zinc sulphide. The full analysis of lithopone takes into account soluble salts of barium and zinc, barium carbonate, and other impurities. For rubber purposes it suffices to determine moisture, acid-insoluble matter, and sulphide. One gramme of the dry material is boiled with concentrated hydrochloric acid diluted with twice its volume of water for half an hour, or until no more hydrogen sulphide is evolved. The liquid is completely cooled and the solid

residue is filtered off, ignited in a platinum crucible, and weighed. A little pure hydrofluoric acid is then added and fumed off, and the crucible is again ignited and weighed ; adulteration with silicates, *e.g.* kaolin, is thus detected. In order to ascertain whether the acid-soluble portion contains non-zinciferous bodies or zinc compounds other than sulphide, the volumetric assay of sulphide described in the next paragraph is carried out on a separate quantity of 0·5 gr. For controlling current deliveries it suffices to decompose with acid and weigh the residue, which should not exceed 70 per cent.

Zinc Sulphide, ZnS (Ger. Schwefelzink, Fr. Sulfure de Zinc), sp. gr. 3·3, has latterly come into vogue as a light pigment of high covering power. The zinc sulphide of commerce is apt to be largely contaminated with relatively less valuable zinc compounds, especially zinc oxide ; some qualities may contain not much more than half their weight of sulphide. It is well, therefore, to determine the content of ZnS in the commercial article, as follows :—0·15 gr. of dried material is weighed into a stoppered bottle and shaken up with 50 c.c. of N/10 iodine solution. Five c.c. of concentrated hydrochloric acid are added and the bottle is allowed to stand, with occasional vigorous shaking, for an hour or two. When decomposition is complete, no white clots should be visible, but only yellow films and skeletons of sulphur. The unused iodine is then titrated back with thiosulphate solution, 1 gr. of iodine being equivalent to 0·384 gr. of ZnS. The better qualities of zinc sulphide should contain not less than 90 per cent. of ZnS. Matter insoluble in strong acid should be absent.

Red Pigments.

Antimony Red, Golden Sulphide (Ger. Goldschwefel, Fr. Soufre Doré d'Antimoine), sp. gr. 3·1—4·2, is one of the oldest and most important accessories of rubber manufacture. Its colouring principle is antimony sulphide in the finely-divided form in which that compound is precipitated from solutions. The smoothness, brilliancy, and high covering power of antimony red make it perhaps the most satisfactory of all rubber pigments.

Antimony red occurs in two main varieties, orange and crimson. The latter, which is little used by itself, is prepared by boiling antimony trichloride with thiosulphate solutions; chemically it is a trisulphide of antimony containing a few per cent. of oxygen, probably in the form of oxysulphide. Tints ranging from crimson through scarlet to orange are obtained by varying the conditions of precipitation, or by mixing orange and crimson sulphides. The orange variety is that which yields the characteristic colour associated in the public mind with red rubber goods. It is prepared by boiling powdered stibnite with polysulphide solutions and precipitating the resulting sulphantimonate solutions with mineral acids. The essential constituent is an antimony sulphide or mixture of sulphides in which the combined sulphur fluctuates between 3 and 3·6 atoms to 2 atoms of antimony. The orange antimony pigment falls into two subdivisions, according as it has been co-precipitated with hydrated calcium sulphate ("plastered antimony") or not. The plastered variety is cheaper to make and, although comparatively poor in antimony, is not so deficient in pigmentary power as might be expected. This, consequently, is on the whole the most popular

form of antimony red. It usually contains from 30 to 50 per cent. of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Not all makes of antimony red keep their colour satisfactorily in vulcanization. This highly important point can be tested only by actual vulcanization experiments. The chemical composition of antimony red is summed up by (1) free sulphur, (2) antimony, (3) calcium sulphate, and (4) sulphide-sulphur.

1. A certain amount of free sulphur is invariably co-precipitated with antimony sulphide. It is for this reason that antimony red was long regarded, erroneously, as in itself a vulcanizing agent, and even now many manufacturers are accustomed to introducing their vulcanizing sulphur into red mixings in this form. Consequently the pigment is commonly supplied as containing so and so much of free sulphur, even up to 40 per cent., the required excess of which is mixed in by the makers. In modern scientific rubber manufacture an exact knowledge of the free sulphur content is, needless to say, indispensable. To determine free sulphur, 2 gr. of antimony red are weighed into a filter-thimble which is plugged with fat-free cotton wool. The material is then subjected to extraction with carbon disulphide in a Soxhlet extractor during eight hours. After evaporation of the solvent, the flask is dried for an hour at 60° before being weighed. The thimble with its contents is also dried, first in the open air, then at 60° . Carbon disulphide, if pure, keeps very well in a red bottle; but if there be any doubt about the solvent, it should be redistilled before being used for extractions.

2. For the determination of metals it is best to take extracted material, because free sulphur, by enclosing particles of unchanged substance, is apt to impede the

dissolving action of acids. Half a gramme of dried extracted pigment is dissolved in 10 c.c. of concentrated hydrochloric acid, and the hydrogen sulphide is boiled off. Two grs. of tartaric acid and 200 c.c. of hot water are added. If there remains a siliceous residue on boiling, this is filtered off and weighed; but there is rarely enough to make it worth while. Antimony is precipitated by means of hydrogen sulphide and may then be determined gravimetrically or volumetrically.

The gravimetric method is on the whole the more trustworthy, especially when antimony determinations are not a daily recurring task. The precipitated sulphide is rinsed from the filter into a large tared porcelain crucible, which is placed on a water-bath. One or two c.c. of concentrated nitric acid are added. During the effervescence which sets in, the crucible is temporarily covered with a watch-glass; the contents are then evaporated to dryness. A few drops of red fuming nitric acid are added to the solid residue, and the crucible is gently warmed over a naked flame, heated more strongly to drive off sulphur and acid fumes, and lastly ignited. The antimony is then present as SbO_2 .

To effect a volumetric determination, the sulphide is rinsed into a beaker and decomposed with concentrated hydrochloric acid. Hydrogen sulphide is driven off by boiling nearly to dryness. The residue is dissolved in water by the aid of tartaric acid and made up to 250 c.c. in a measuring-flask. Of this solution 100 c.c. are neutralized with sodium carbonate, cooled, rendered alkaline with 10 c.c. of saturated sodium bicarbonate solution, and titrated with $N/10$ iodine solution. Antimony can also thus be determined directly in the extracted or (provided there be no difficulty in dissolving) in the original pigment. One gr. of I corresponds to 0.473 gr. of Sb.

3. The filtrate from the precipitated sulphide is rendered alkaline with ammonia. A little iron may here present itself as a green colloidal solution of ferrous sulphide; this is coagulated by boiling and filtered off. The iron itself is of no great importance, but it must be removed before precipitation of calcium, which latter, on account of the high factor of conversion, needs to be determined with precision. Calcium is brought down as usual by means of ammonium oxalate and is weighed as CaO.

4. It is not practicable to determine sulphide-sulphur directly as such. Instead, total combined sulphur is determined in the extracted pigment and the necessary deductions for calcium sulphate are subsequently made. Either of the following methods may serve:—

(a) Not more than $\frac{1}{2}$ gr. of extracted substance is dropped little by little into 5 c.c. of concentrated sulphur-free nitric acid contained in a 50 c.c. Erlenmeyer flask. The acid is meanwhile kept cool by shaking the flask in a basin of water. Antimony is thus completely oxidized, but a certain amount of sulphur remains in the form of yellow clots. The flask is now gently heated on a water-bath, care being taken to avoid fusion of the sulphur, and a pinch of powdered potassium chlorate is added from time to time until all the sulphur has disappeared, whereupon the mixture is transferred to a small basin and evaporated on the water-bath nearly to dryness. The residue is lixiviated with hot water; the filtrate, which should be made up to about 400 c.c., is boiled up with the addition of a little hydrochloric acid (and tartaric acid, if necessary), and barium sulphate is brought down in the usual way.

b. The potash-peroxide fusion method (*cf.* p. 131) is very expeditious and not less accurate than any other. The substance (0·3 to 0·5 gr.) is melted down in an iron

bowl with 5 gr. of stick potash and about 1 c.c. of water. When the melt no longer effervesces on addition of a little sodium peroxide, enough peroxide to produce the dark ferrate colour is added and thoroughly melted in. On lixiviation, acidification with hydrochloric acid, and boiling, it sometimes happens that everything goes into solution. More usually, however, there is a flocculent antimonial residue, which is filtered off. The clear liquid is precipitated with barium chloride as usual.

Analyses of antimony red, conducted as above, are rather apt to give figures adding up to more than 100. This is often, if not mostly, due to the calcium sulphate being present in an aggregate state of hydration falling short of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Some typical analyses of antimony reds :—

	Orange, English I.	Orange, English II.	Orange, French.	Orange, German.
Free Sulphur	19·1	17·9	7·3	15·2
Antimony	23·5	22·2	62·3	54·7
Sulphide-Sulphur	11·2	10·3	27·5	25·0
Calcium Sulphate	46·4	50·4	3·2	5·3
	100·2	100·8	100·3	100·2

	Scarlet, French.	Crimson, English.
Free Sulphur	10·6	15·6
Antimony	41·4	62·1
Sulphide-Sulphur	17·8	19·6
Calcium Sulphate	30·6	—
Oxygen (by difference)	—	2·7
	100·4	100·0

Moisture in antimony red is determined upon 5—10 gr., not by oven-heating, but by drying in a vacuum exsiccator. Normally it should not exceed 1 per cent.

Acidity may be determined as in sulphur (see p. 92), except that the titration is performed on an aliquot portion of clear liquid, e.g., one-half of the total volume, decanted from the solid matter. Calculated as H_2SO_4 , it should not exceed 0·06 per cent.

Running deliveries of antimony red should be watched for uniformity of colour. Free sulphur should invariably be determined and it is well, also, to check the contents of antimony and plaster by the following handy method due to F. Jacobsohn¹ :—

1. One gr. of pigment is oxidized in a porcelain crucible with a few c.c. of fuming nitric acid, evaporated, and ignited. This gives SbO_2 plus $CaSO_4$.

2. One gr. of original pigment (not, as proposed by Jacobsohn, of the oxidized matter from the above operation) is mixed in a porcelain crucible with 2 gr. of resublimed ammonium chloride, fumed off, and ignited. Antimony being thus volatilized, there remains $CaSO_4$ plus any siliceous matter present. A slight conversion of calcium sulphate into chloride may take place, but not enough to disqualify the method for technical use.

Rouge, Oxide of Iron, Fe_2O_3 (Ger. Eisenoxyd, Fr. Oxyde de Fer), sp. gr. 5·0—5·2, is inferior in attractiveness to antimony red, giving at best dull and brownish tones. Its chief uses are for non-poisonous articles ; for ebonites, in the vulcanization of which it behaves better than antimony red ; and for heat-resisting goods generally. Rouge is prepared by calcining iron sulphate, and the better qualities are almost chemically pure ferric oxide. A

¹ *Chem.-Ztg.*, 32 (1908), p. 984.

number of rouges supplied as rubber pigments, however, contain much added matter. To produce a more brilliant colour, the rouge is often calcined in company with calcium or barium sulphate, and calcium carbonate or other diluent is sometimes added, so that rouges containing as little as 30 per cent. of Fe_2O_3 are not unknown.

Rouge is examined as follows. Iron is determined by boiling 0·5 gr. with 500 c.c. of hydrochloric acid (1 : 20), adding excess of ammonia, and filtering off and igniting the precipitate plus undissolved residue. Silica is then detected by evaporating with hydrofluoric and sulphuric acids, igniting, and re-weighing. The filtrate is divided into equal halves, and in the one calcium is determined, in the other sulphuric acid. Barium sulphate, if present, can generally be observed as a heavy white admixture when the pigment is boiled up with acid; it is separated from ferric oxide by fusing with potassium bisulphate and leaching out the iron with hot dilute acid. Rouge is subject to considerable variation in tint, according to the mode of preparation; the pigmentary effect of a given specimen in the rubber can be judged with certainty only by experimental vulcanizations. The colour of running deliveries should be controlled by painter's test.

Red Ochre, a pigment prepared by calcining yellow ochre (see p. 83), is practically a rouge much diluted with siliceous matter and is consequently of inferior covering power.

Vermilion, HgS (Ger. Zinnober, Fr. Vermillon), sp. gr. 8·1, is by far the most brilliant and powerful of red pigments, but also one of the most costly; its use is limited to very special articles, such as dental rubbers. It should be tested for free sulphur and ash, both of which should be practically absent. The presence of soluble mercury

salts is easily detected, and should on no account be tolerated. Vermilions are occasionally adulterated with organic dyestuffs to heighten the colour.

Black Pigments.

Lampblack, amorphous carbon (Ger. Russ, Fr. Noir de Fumée), sp. gr. 1·8, is the soot prepared by burning oily, resinous, and tarry matter, natural gas, or acetylene. Carbon in one form or another is the only black pigment (excepting lead sulphide, cf. p. 64) suitable for rubber. Different makes of lampblack vary enormously in bulkiness, but they are much alike in covering power, weight for weight. Lampblack should be assayed for greasy matter by extraction of 1—2 gr. with acetone, and also for ash; gritty particles contained in the latter are to be regarded as deleterious. With the bulkier sorts of lampblack, acetone extraction is best carried out thus:—2 gr. are shaken with acetone in a 100 c.c. flask and made up to about 1 c.c. above the mark. Should a persistent suspension be formed, a drop of dilute hydrochloric acid may be added to effect coagulation. After settling (which may be hastened by means of the centrifuge), 50 c.c. of the clear liquid are pipetted off and evaporated in a tared Soxhlet flask.

Good qualities of lampblack show up to 5 per cent. of grease and mere traces of ash. Inferior grades may contain several per cent. of mineral matter and may possess a brownish discolouration, which is sometimes cloaked by means of ultramarine or other blue pigment.

Bone-black, which is a product of charring, not of combustion, consists of amorphous carbon together with calcium phosphate and carbonate. The mineral matter usually amounts to about 90 per cent.; owing to its pre-

sence and to a certain coarseness of grain, the application of bone-black is comparatively limited. The percentage of carbon may be approximately arrived at by determining ash and acetone extract. It is more accurate, however, to determine carbon directly by dissolving out mineral matter with hydrochloric acid and weighing the residual matter on a tared filter ; the ash of this residue is then determined and deducted.

Black Hypo is less in vogue now than formerly ; it is a complex mixture of varying composition, prepared by calcining litharge together with sulphur, with or without the subsequent addition of bone-black or lampblack. Beside litharge and lead sulphide, black hypo contains the lead salts of several sulphur oxy-acids. Analysis yields little information as to its value in rubber mixings ; but the content of free sulphur should invariably be determined.

Graphite (Ger. Graphit, Fr. Plombagine), sp. gr. 2·2 upwards, is in request rather as a filler than as a pigment. It has a considerable stiffening effect, and its remarkable lubricating properties, by preventing the rubber from sticking to metal, render it valuable in steam-jointings and other high-temperature goods. Like talc it serves, with certain classes of goods, for pouncing doughs and moulds. Graphite is supplied in widely varying degrees of purity, according to the amount of associated earthy matter, which ranges from one or two per cent. to thirty or forty per cent. The value of a graphite is in general proportional to its content of graphitoidal carbon. The degree of fineness, also, is not a matter of indifference. Flake graphites, which can scarcely rank as black pigments, are more highly prized than powder graphites, on account of their mechanical properties. Chemical ex-

amination need seldom be carried beyond an assay of the carbon, which is effected with sufficient accuracy for most purposes by incineration in a platinum crucible. Carbon in the form of graphite burns away very slowly, and it is advisable to turn over the powder occasionally during ignition. High-class flake graphites containing very little ash cannot be dealt with by open incineration, but must be placed in a boat and burnt with the aid of oxygen in a small tube-furnace.

Other Pigments.

Yellow, green, and blue pigments are of minor importance. Their chief use is for toys, surgicals, and tiling; latterly also yellow pigmentation has come into some prominence in connexion with balloon fabrics. Beside mineral pigments, a number of organic dyestuffs are in use for uncured and cold-cured goods, especially in the form of superficial applications. The most brilliant effects are obtained with dyes soluble in naphtha, which are incorporated with the rubber in the form of solutions. To some extent, also, organic dyes are employed in the form of lakes deposited upon alumina, barium sulphate, &c., which are added to the mixings as powders. Organic dyes for use in rubber should be resistant to acids and totally insoluble in water.

Yellow Ochre is a natural product, consisting of clayey and other siliceous matter with 20—30 per cent. of hydrated iron oxide. It is not a strong pigment and lacks brilliancy. *Chrome Yellow*, PbCrO_4 , is very satisfactory as a colour in the rare cases when its lead content permits it to be used. *Cadmium Yellow*, CdS , is much the best yellow pigment, as it gives a fine colour and is not in the least affected by vulcanization; but it is about

as dear as, or dearer than, rubber itself. *Precipitated Arsenic Sulphide*, As_2S_3 , is an excellent pigment and resists heat-curing, but has the defect of being extremely poisonous.

Chrome Green is the chief green pigment of general applicability. It consists almost wholly of chromium sesquioxide, and is quite indifferent to vulcanization. *Rinmann's Green* (zinc-cobalt oxide) is also in use for cold-cured goods.

Prussian Blue and *Ultramarine* serve as blue pigments, the latter being preferred owing to its greater permanency. Where resistance to acids is essential, ultramarine is out of court ; Prussian blue, on the other hand, is decomposed by alkalis, and is also somewhat apt to suffer in vulcanization.

CHAPTER V

MISCELLANEOUS ACCESSORIES

Naphtha.

VAST quantities of rubber solvent are used up in the manufacture of rubber goods. By making rubber, previously mixed with compounding materials, into a treacly "solution" with naphtha, textile threads and fabrics can be so impregnated or coated that the rubber adheres in a continuous form after evaporation of the solvent and vulcanization. The "proofing," *i.e.* waterproofing, of fabrics in this manner is one of the very oldest branches of the rubber industry. In more recent times impregnation by means of solutions has come to play an important part in the manufacture of composite objects such as tyres, hose, belting, overshoes, &c. The only rubber solvents economically applicable on the large scale are coal-tar (benzenoid) and petroleum (paraffin and olefine) hydrocarbons. *Petroleum, or Mineral, Naphtha* (Ger. Benzin, Fr. Essence Minérale), once largely used, is a medium in which rubber does not swell so readily as in benzene homologues, but has the advantage of being less apt to impart a foreign odour to the goods; it has now-

adays fallen very much into the background, mainly owing to considerations of price. The popular rubber solvent is *Coal-Tar Spirit* (Ger. Benzol, Fr. Essence de Houille), especially the xylene fraction, known in the trade as *solvent naphtha*, which is not excessively volatile in the open air. Solvent naphtha generally boils to the extent of 95 per cent. between 125° and 155°, and consists principally of the three xylenes flanked by minor proportions of toluene, pseudocumene, and mesitylene. This is not, however, the only coal-tar fraction which finds application in rubber manufacture. In a smaller way, "nineties" benzene (B.P. 80°—120°), of which 90 per cent. distils up to 100°, and "fifties" benzene (B.P. 80°—130°), of which 50 per cent. distils up to 100°, are also used.

Specific Gravity.—The determination to three places of decimals is effected with great ease and rapidity by means of hydrometers (see Chap. VI). Standard temperature is largely a matter of convention: 15° is on the whole the most usual for density statements, but 18° and 20°, as being more convenient practically, are also favoured. If determined at some other known temperature, specific gravities can be corrected to standard by the aid of coefficients of expansion (see p. 102). Specific gravities serve chiefly as a rough preliminary test to detect irregularities; also, they afford valuable indications as to the presence of coal-tar naphtha in petroleum naphtha, or *vice versa*, since benzenoid hydrocarbons are considerably heavier than paraffin hydrocarbons of about the same boiling-point. The specific gravity of solvent naphtha is 0·860—0·870 at 15°; that of nineties benzene (0·880—0·885) and that of fifties benzene (0·870—0·880) are slightly higher.

Distillation Test.—All naphthas, whether single samples or running deliveries, should be examined by distillation. The quantitative results of fractional distillation vary considerably according to the *modus operandi*. Placing the thermometer in the boiling liquid, for instance, affects the results in one sense, and the use of an efficient dephlegmator in the opposite sense. Whenever it is necessary to compare figures with those obtained by some standardized method, the prescribed form of apparatus and procedure must be adopted. For general purposes, however, one may as well employ the most accessible form of apparatus and the simplest and least unscientific mode of distillation. The following procedure may be recommended :—

One hundred c.c. of naphtha are introduced into an ordinary distillation-bulb of 150 c.c. capacity, which is fitted with a thermometer (bulb about half-way down the vapour-column) and connected to a rather short Liebig's condenser having an inner tube of uniform diameter from end to end. A few grains of pipeclay or pumice are added and the naphtha is distilled, over a steady flame, into a 100 c.c. measuring-jar at about the rate of two drops per second. The stem of the distillation-bulb should be 16—20 mm. wide and its height between bulb and tubulure 70—80 mm. The exact initial temperature of distillation is of no significance, because the first few c.c. of distillate are always contaminated with water and have therefore an abnormally low boiling-point. The thermometer is imagined divided into spaces of 5° above and below 100°; as soon as the first of these points after commencement of distillation has been reached, the volume of distillate is read off and is regarded as belonging to the preceding interval of 5°. For example, if nothing

has begun to come over at 115° , but 9 c.c. have been collected when the thermometer reaches 120° , then 9 c.c. are set down as coming over in the interval 115° — 120° . As distillation proceeds, readings of the volume distilled are taken every 5° , and the quantity coming over between each point is calculated by subtraction. In this way a lucid and comparable picture of the composition of the naphtha is obtained. Distillation is continued up to 95 or 96 per cent. of the total volumes.

The following figures represent distillation-tests of typical solvent naphthas :—

	I.	II.	III.	IV.
110° — 115°	—	—	3	—
115° — 120°	—	—	13	—
120° — 125°	2	—	21	9
125° — 130°	19	3	16	15
130° — 135°	23	18	15	23
135° — 140°	30	38	12	19
140° — 145°	17	25	8	13
145° — 150°	4	9	5	9
150° — 155°	2	2	3	5
Above 155°	3	5	4	2 (155° — 160°)
	100	100	100	5 (above 160°)
				100

For purposes of rubber manufacture the initial boiling-point matters little, except in so far as the naphtha will be more volatile in the open air, the lower it is. Naphtha III is rather exceptional, containing, as it does, a very considerable proportion of toluene. More importance attaches to the final boiling-point. The highest boiling fractions are comparatively difficult to dry out of the rubber, and are then apt to give trouble by retarding vulcanization. Moreover, they often contain malodorous bodies which impart an obstinate smell to the finished

goods. Hence it is a sound rule to reject naphthas of which more than 5 per cent. boils above 155°. Many naphthas, like IV, are currently used, of which 5 per cent. or so boils above 160°; but if a temperature-limit is to be set at all, it had better be set at 155°.

The residue in the distillation-bulb is turned into a dish and allowed to evaporate in the open with little or no heating. Any excessive amount of greasy matter in solution will thus reveal itself, and naphthalene, if present, will be left in the form of crystals. Naphthalene is to be regarded as an undesirable impurity, on account of its clinging smell. Impurities due to inadequate refining, such as phenols and pyridines, are detected by their odour when the naphtha is allowed to evaporate on filter-paper or on the palm of the hand. Carbon disulphide, which, however, rarely occurs, may be tested for as below.

The more volatile coal-tar naphthas, nineties or fifties benzene, commercial toluene, &c., are subjected to distillation-test in the same way. Being fractions which come over, in the coal-tar distilleries, before solvent naphtha is collected, they usually boil to the extent of 95 per cent. below 130°. They are very liable to contain carbon disulphide, an impurity which is objectionable, not indeed on technological, but on hygienic, grounds. To determine carbon disulphide, about 1 c.c. of phenylhydrazine is added to 100 c.c. of the naphtha, and the liquid is allowed to stand for at least ten hours. A voluminous crystalline deposit of the phenylhydrazine salt of phenylthiocarbazidic acid separates out; this is filtered off, air-dried, detached from the filter, and weighed. By applying the factor 0·26 the weight of carbon disulphide is found. No naphtha intended to be used in workshops where it is evaporated into the atmosphere should contain more than

2 gr. of carbon disulphide per litre. This and other malodorous impurities are also highly undesirable in rubber solutions intended for sale.

Petroleum Naphtha occurs in a greater variety of ranges of boiling-point than coal-tar naphtha. Much, if not most, of that which comes into the rubber industry boils between 80° and 140°. Any residue above 140° will consist, in part, of heavy matter having the character and smell of lamp-oil, and should therefore be kept low. On the other hand, a large proportion distilling below 100° is not less undesirable, on account of its volatility in ordinary handling. Distillation tests are made exactly as with coal-tar naphtha.

Shale Naphtha is a rubber solvent which, being produced in limited quantity, seldom travels far from its place of origin (Midlothian and Lanarkshire, in the British Isles). It is composed of olefine and paraffin hydrocarbons in approximately equal parts, and commonly boils between 75° and 155°.

Carbon Disulphide (Ger. Schwefelkohlenstoff, Fr. Sulfure de Carbone) is used as a diluent and impregnating agent in the cold-cure process; it boils at 46°—47° and has a specific gravity of 1·27. Commercial carbon disulphides are frequently not far from chemically pure, but the inferior grades contain traces of organic sulphur-compounds which give them a villainous odour, and sometimes a more or less yellow tint. Unless freshly rectified, carbon disulphide invariably holds a slight amount of sulphur in solution, which is easily determined by distilling 100 c.c. out of a tared flask. For rubber work, carbon disulphide should not be grossly malodorous, and should show at most 2 gr. of distillation-residue per litre.

Carbon Tetrachloride (Ger. Tetrachlorkohlenstoff, Fr.

Tétrachlorure de Carbone) serves, alone or mixed with coal-tar naphtha, for making non-inflammable rubber solutions, and also as a diluent in the cold-cure process. The pure substance, sp. gr. 1·63, boils at 77°. Good commercial carbon tetrachloride should distil between 75° and 78°, and leave no residue. Adulterations with hydrocarbons are best detected through the specific gravity. From its mode of manufacture, carbon tetrachloride is usually contaminated with carbon disulphide; this is detected and determined as in coal-tar spirit.

Vulcanizing Agents.

Next to rubber itself the most important raw material of the rubber industry, though not necessarily the one used in largest quantity, is sulphur. When mixed with sulphur and heated to temperatures above 120°, raw rubber enters into chemical combination with a greater or less amount of sulphur and so becomes *vulcanized*. The product, vulcanized or "cured" rubber, differs from the uncured material in that it is stronger mechanically, is insoluble (though it swells up to some extent) in rubber solvents, is practically indifferent to changes of temperature within fairly wide limits, and is a more stable substance generally. The discovery of vulcanization in the early forties of last century may be regarded as the true starting-point of rubber manufacture on the large scale.

Sulphur for rubber mixings takes the form, for the most part, of *Flowers of Sulphur* (Ger. Schwefelblumen, Fr. Fleurs de Soufre), sp. gr. 2·0. This is a fine powder obtained by sublimation and consists of a mixture of ordinary λ -sulphur and μ -sulphur, the latter of which is insoluble in carbon disulphide and makes up about three-quarters of the flowers. Coarse mechanical impuri-

ties being supposed absent, flowers of sulphur always contain free sulphuric acid and a little moisture. The latter is determined by drying 5 gr. on a flat dish in a vacuum-exsiccator. To determine acidity, 10 gr. are mixed with enough alcohol (previously neutralized) to moisten the powder thoroughly; 100 c.c. of water and some phenolphthalein are added and titration is carried out with $N/10$ caustic soda solution. There should not be present at the very outside more than 0·2 per cent. of acid, calculated as H_2SO_4 . Flowers of sulphur are practically free from ash; any notable incineration-residue will be due to adulterations, *e.g.* with infusorial earth. A finer but more expensive form of sulphur, which is used in comparatively small quantities, is *Precipitated Sulphur*. This should contain not more than 0·05 per cent. of free acid and 1 per cent. of ash. In some varieties there is an admixture of calcium sulphate, due to the process of manufacture. Precipitated sulphur is apt to contain several per cent. of moisture. Another form of sulphur sometimes met with is a greenish powder, which is obtained by grinding impure solidified sulphur and shows up to 10 per cent. of ash consisting of ferruginous clayey matter. In addition, a number of mixtures under fancy names are, or used to be, on the market; these very commonly contain paraffin or other waxy matter and various mineral loadings.

Sulphur is also employed in rubber works for sulphur-baths, *i.e.* baths of molten sulphur in which articles to be vulcanized are immersed either naked or in moulds. The sulphur in the latter case acts merely as a carrier of heat, in place of the more usual high-pressure steam or hot air. Sulphur for use in baths is bought in stick or lump form and need be examined only for ash.

Sulphur Chloride, S_2Cl_2 (Ger. Chlorschwefel, Fr. Chlorure de Soufre), sp. gr. 1·68, is another body possessing the property of combining with rubber to produce a material which closely resembles sulphur-vulcanized rubber in physical respects. Unlike sulphur in elementary form, sulphur chloride acts instantaneously in the cold; consequently the vulcanizing effects obtainable by it are only skin-deep. Vulcanization by means of sulphur chloride, or "cold-curing," was discovered a few years later than heat-curing and is still much practised, though necessarily on a somewhat restricted scale. Sulphur chloride is usually applied to the articles to be cured (*i.e.* thin sheet, tubing, or thread, proofed fabrics, &c.) in dilute carbon disulphide or carbon tetrachloride solution. It is also applied in the form of vapour, by which method peculiarly glossy surfaces can be produced. Moisture or moist air must be rigorously excluded in any process in which sulphur chloride comes into play.

Sulphur chloride should always be examined by distillation. The boiling-point of the pure substance, *viz.*, 137°, is greatly affected by impurities. In a reasonably pure commercial article, a range of 130°–140° may be allowed, with a residue of 5 per cent., which may consist principally of sulphur. Dissolved sulphur is determined by rinsing this residue with carbon disulphide into a tared Soxhlet flask, drying at 110°, and weighing. The commonest impurities are either chlorine (in the form of SCl_2), which is highly noxious, or dissolved sulphur, which in small amount is harmless. Too much dissolved sulphur, *e.g.* more than 5 gr. per 100 c.c., may cause the cured goods to sulphur up. On the assumption that no elements other than sulphur and chlorine are

present, excess of either may be determined by C. O. Weber's¹ method, as follows :—

A solution of the material is first prepared by accurately weighing about 5 gr. into a 100 c.c. flask and making up to the mark with dry benzene. Of this solution, 10 c.c. are pipetted into 25 c.c. of *N/1* alcoholic potash solution in a wide-mouthed flask. The mixture is digested on a water-bath for an hour, whereupon the solvent is distilled off and expelled by heating the flask in the oven at 110°. The residue is taken up with 100 c.c. of hot water and rendered slightly acid with nitric acid. Ten c.c. of a 10 per cent. copper sulphate solution are added to eliminate sulphide-sulphur, and in the filtrate chlorine is determined gravimetrically in the usual way. Chemically pure sulphur chloride contains 52·5 per cent. of chlorine.

Should naphtha, or carbon disulphide or tetrachloride, be present, the above method might lead to erroneous conclusions. Such impurities, however, are likely to occur only in recovered sulphur chloride. They may easily be detected by decomposing the sulphur chloride with a large excess of dilute aqueous caustic soda solution and submitting the liquid to distillation. The impurities in question will then come over with steam in the first runnings, and may be measured and identified.

Oils and Waxes.

Various oils, both glyceride and hydrocarbon, play a modest part in the compounding of manufactured rubber. Oils serve on the one hand to facilitate the mixing and sheeting of low-grade doughs, and on the other hand to impart a certain softness and suppleness to the finished goods. They are added in quite small proportions,

¹ *The Chemistry of India Rubber*, London, 1902, p. 182.

seldom exceeding 5 per cent. of the rubber. The glyceride oils most in use are *linseed*, *cottonseed*, *rape*, and *castor* oils. As a rule no special chemical examination is required, provided the oil be what it purports to be.

Mineral Oils ranging from light spindle oil to semi-solids of the vaseline type are used for much the same purposes as the above, and in similar small doses. It is well to test mineral oil for free acid, *i.e.* sulphuric acid introduced by the refining process. In the case of pale oils this is done by shaking up 10 gr. of material with a previously neutralized mixture of alcohol and ether (4 : 1) and titrating with *N/10* caustic soda and phenolphthalein. With dark oils the phenolphthalein colour-reaction by this method is almost or completely obliterated. If too dark for direct titration, the oil is well shaken with three 20 c.c. lots of hot 90 per cent. alcohol (previously neutralized), and the united alcoholic extracts are titrated with phenolphthalein as indicator. Or the oil may be directly titrated in ether-alcohol solution with the aid of Alkali Blue 6 B (Höchst), an indicator which strikes blue with acid and red with alkali.

Mineral Waxes, viz., paraffin (made from petroleum, shale, or lignite) and ceresine (made from ozokerite), are very extensively added to rubber mixings in small proportions, the maximum being about 10 per cent. on the rubber. In soft rubber goods generally, the effect aimed at is reduced micro-porosity, whence increased air- and water-tightness; in cable-coverings mineral wax serves the further purpose of enhancing insulation-resistance. Although ceresine and paraffin are closely similar chemically, they differ widely in consistency, ceresine having a tough, amorphous structure like beeswax, whilst paraffin

is "short" and subcristalline. The specific gravity of all these waxes varies between 0·89 and 0·92.

Mineral waxes, provided they melt to clear white or yellowish liquids, are unlikely to contain deleterious impurities. The temperature at which they liquefy is a matter of no great moment from the rubber point of view, but is important on the score of cost, since mineral waxes are mostly sold on a melting-point basis, the highest-melting ones being the most prized. *Ceresines* of the best quality show melting points approaching 75°; the medium qualities, M. P. 60°—70°, are mostly mixtures of true ceresine with paraffin; cheap grades are apt to be adulterated with rosin. Paraffin may be approximately determined by E. Graefe's¹ method based on the partial precipitation of ceresine (but not paraffin) from carbon disulphide solutions by ether-alcohol. Rosin is isolated quantitatively by boiling out with alcoholic potash.

The best hard *paraffins* melt at a few degrees above 60°, and qualities melting down to 50° are current which are still hard and homogeneous; the lower-grade varieties, such as *paraffin scale*, contain a small amount of heavy mineral oil which beyond certain limits does not form a homogeneous solid solution, but is ready to exude on to any absorbent surface. These oily paraffins, in fact, represent a transition-stage between hard paraffin and vaseline.

The melting-points of mineral waxes are anything but sharp, and it is impossible to obtain comparable results unless a standard method be adopted. On the whole the most serviceable method hitherto proposed is that of L. Ubbelohde;² it requires, indeed, a special form of apparatus, but in return yields definite and reproducible

¹ See J. Marcusson and H. Schlüter, *Chem.-Ztg.*, 31 (1907), p. 348.

² *Zt. Angew. Chem.*, 18 (1905), p. 1220.

figures. A thermometer A (Fig. 17) and a tiny glass funnel B are so connected by a split brass tube C that the thermometer-bulb always occupies a fixed position with respect to the funnel when the latter is pressed home. The funnel is charged with melted wax and attached to the thermometer before the wax has set. The whole apparatus is then fixed in an air-bath consisting of a test-tube of 4 cm. diameter and 23 cm. length, which dips into a large beaker of water. Heat is applied in such a way that the thermometer rises about 1° per minute. The temperatures at which the wax commences to sag out of the bottom of the funnel (softening-point) and at which the first drop of molten material disengages itself (dropping-point) are both noted ; they may lie from 2° to 6° apart.

Fabrics.

The textile fabrics which come into use in rubber manufacture are mostly of cotton, and in a few cases of flax or hemp. They range from fine dense tissues for surgical sheeting and waterproof garments to the coarsest ducks for belt and tyre insertions. The suitability of a fabric for a given purpose is mainly a question of weight per unit area, spacing and thickness of threads, strength, and behaviour under heat. Chemical examination is concerned chiefly with such sizing preparing, and loading materials as may be present, any of which is undesirable in excessive amount. *Sizing* is determined by extracting 5 gr. of air-dry fabric with hot

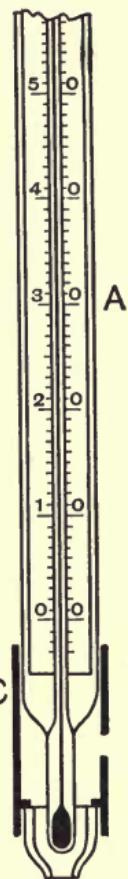


FIG. 17.

water and evaporating and drying the filtrate on a flat porcelain dish ; 4 per cent. of aqueous extract may be allowed. *Greasy matter* is extracted out of 10 gr. by means of carbon disulphide ; it is usually under 1 per cent. and should not exceed 2 per cent. *Mineral loading*, apart from the small amount of mordant which may occur in dyed fabrics, should be altogether absent ; its presence is revealed by the results of incineration, allowance being made for the fact that 1—2 per cent. of ash is a normal constituent of undyed cotton. The ash should in any case be free from copper.

CHAPTER VI

SPECIFIC GRAVITIES

THE specific gravity, or density, of a substance is strictly defined as the weight *in vacuo* of a cubic centimetre of the substance. In practice it is usual to define it as the weight in air of the substance divided by the weight in air of an equal volume of water at 4°. The error thus involved is insignificant for practical purposes. Liquids have comparatively high coefficients of expansion, and their densities should never be stated without specifying the exact temperature; with solids at ordinary temperatures there is no need for any such refinement.

Liquids.

Organic solvents and oils are the liquids of which the density is of most interest in rubber manufacture. There are three instruments for determining the densities of liquids: in ascending order of convenience and descending order of precision these are (1) the pycnometer, (2) the hydrostatic balance, and (3) the hydrometer. For technical purposes hydrometers are the most generally useful, on account of the ease and despatch with which determinations are made. Those on which specific

gravities are directly read off are much to be preferred. A hydrometer, if properly made and calibrated, should give results correct to 0·001 of specific gravity. To attain this degree of accuracy, it must have a scale sufficiently open to be divided visibly into 0·001 units ; consequently there must be available not one but several spindles, each with a short range of 0·06 or 0·1 of specific gravity. For solvent naphthas 0·800—0·900 or 0·820—0·880 will be the range ; for petroleum naphtha 0·650—0·800 in two or more spindles. Very long spindles are unhandy ; 20 cm. is a convenient length. The scale-marks of a bought hydrometer should never be taken on trust. Calibration is effected as follows :—

Two liquids, pure or mixed, are chosen such that their densities correspond to points near either end of the scale. Their temperature having come into equilibrium with that of the room, readings of the hydrometer are taken when floating in each ; the exact density of each is then determined by means of the pycnometer, care being taken that there has been no change of temperature in the meantime. The whole operation should be repeated at least once, preferably at another temperature. If now it is found that the difference, for the two liquids, between the hydrometer results is not the same (to within 0·001 of specific gravity) as the difference between the pycnometer results, it will be necessary to draw up a full table connecting scale-readings with true specific gravity ; on the whole, however, it is simpler to reject the hydrometer. If these differences are identical, but there is a constant discrepancy between scale-readings and true specific gravity, then this discrepancy is noted as a correction to be applied to the hydrometer readings ; it may conveniently be recorded on the hydrometer-case. If, lastly,

this discrepancy does not amount to 0·001, then the hydrometer is as accurate as such an instrument can be.

Hydrometer readings should be observed from below the level of the liquid, with the spindle floating freely out of reach of the walls of the vessel. About 300 c.c. of liquid should be taken, in a cylinder at least 5 cm. wide. It is well to stir up with the thermometer before introducing the spindle.

The hydrostatic balance (Mohr's balance) has for its principle the weighing of a glass plummet, commonly of 5 or 10 c.c. displacement, when suspended in the liquid under test. This is done either by laying ordinary weights on a pan or by means of riders corresponding to 0·1, 0·01, 0·001, &c., of specific gravity, which are adjusted on a beam bearing a scale of ten divisions. Whatever be the form of apparatus used, it should be so designed that specific gravities are read off directly. Calibration is easily effected by means of distilled water, and there is generally no difficulty in meeting errors of instrument by making an alteration on the balance itself rather than applying corrections. Mohr's balance is available for liquids of any density, and has the advantage of working with small quantities—50 c.c. or even less—of liquid. It may be relied upon for three places of decimals; a yet higher accuracy can be attained, but only by taking special precautions with regard to the suspension-wire of the plummet.

The pycnometric method consists in the weighing of a vessel of known volume when filled with the liquid. By the use of pycnometers of the Sprengel tube type, and temperature-adjustment in a thermostat, the method may be driven to an accuracy of 0·00001, but it is useful also on a lower level of precision for check determinations, for

calibrating hydrometers, and for determining the specific gravity of solids (see below). Pear-shaped pycnometers with perforated ground-in stoppers—the specific gravity bottles of commerce—may be conveniently employed, and they should be calibrated in grammes of water at 4°. Counterpoises are usually supplied with these vessels and are a great boon, but it is imperative to adjust them from time to time. The most generally suitable sizes of pycnometer are from 10 to 50 c.c. For taking the density of liquids a 10 c.c. capacity suffices, and, if the volume happen to be exact to within a milligramme, determinations involve no calculation whatever. Very viscous liquids should invariably be dealt with by pycnometry, the other methods described above being unsuitable.

It often occurs that the density D_T at a standard temperature T° is required, but that it is experimentally more convenient to determine the density D_t at a not too remote temperature t° . If the coefficient of expansion k of the liquid (see Appendix, Table V) be known, the requisite correction is given by the formula

$$D_T = D_t \{1 + k(t - T)\}$$

Pulverulent Solids.

Matter in the solid state presents an important distinction between true and apparent specific gravity: the former refers to the volume actually taken up by the solid material and nothing else, the latter to the volume outlined by a solid which may enclose air in vacuoles or cushioned between discrete particles. Thus the apparent specific gravity of a spongy mass or a fluffy powder may be as little as a tenth, or less, of the true specific gravity.

For determining the true specific gravity of powders

the most generally applicable method is the pycnometric one. A pear-shaped 50 c.c. pycnometer is charged with about one-quarter its capacity of substance and weighed. Enough water to half-fill the vessel is added and thoroughly shaken up with the powder. The vessel is warmed on a water-bath to about 50°, placed under a bell-jar or in an exsiccator, and subjected to evacuation until the water boils briskly; when this point is reached the vacuum must be more cautiously regulated to avoid spilling. After its contents have been in ebullition for some minutes, the pycnometer is cooled, filled up with water, stoppered, and weighed, the temperature of the water being noted. An alternative procedure is to weigh the powder into a beaker, boil over the flame with a small quantity of water, cool, rinse into the pycnometer, and continue as above. It is of course assumed that the powder is neither insoluble in, nor otherwise affected by, water; otherwise recourse must be had to alcohol, benzene, or other mobile liquid, the density of which must be accurately determined. Calculations are made by the formula :—

$$\text{Sp. Gr.} = \frac{W_1 \cdot d}{W_2 - W_3 + W_1}$$

where W_1 = weight of solid

W_2 = weight of liquid, aqueous or otherwise, filling the pycnometer, the solid being absent.

W_3 = weight of solid plus liquid filling the pycnometer.

d = density of liquid at temperature of experiment, against water at 4°.

The result, it will be observed, is referred not to c.c. but to grammes of water at 4°; the difference, however,

vanishes in the experimental uncertainties, nor need the thermal expansion of the powder be taken into consideration. Owing to the difficulty of disengaging the entangled and adsorbed air from a powder it is seldom possible, unless very refined methods be applied, to state more than two places of decimals accurately in the specific gravity. Generally speaking, organic liquids have the property of wetting solids better than water, and therefore drive out the air more effectively. Thus for sulphur, graphite, etc., or fine greasy powders, water cannot satisfactorily be used.

A second method, as accurate as the above but less widely applicable, consists in floating the powder in a liquid having the same density as itself. The powder is shaken up in a cylinder, or boiled if necessary, with a liquid heavier than itself, which is then diluted with a light liquid until the powder rises. When the mixture has been so adjusted that the bulk of the powder floats between the bottom of the vessel and the surface of the liquid, the specific gravity is taken *in situ* by means of Mohr's balance. The method fails with powders which are mixtures or which have a specific gravity exceeding 3·3. Heavy liquids available for this method are:—

Cadmium boro-tungstate, sp. gr. 3·28, to be diluted with water. Attacks carbonates.

Methylene iodide, sp. gr. 3·33, to be diluted with benzene. May be decolorized, at need, by shaking with mercury.

Potassio-mercuric iodide, sp. gr. 3·19 (54 pts. HgI_2 , 43½ pts. KI, 10 pts. water), to be diluted with water.

India-Rubber, etc.

The method in general use for ascertaining the specific gravity of rubber, resins, pitches and waxes is that of

hydrostatic weighing, which is fairly expeditious and leaves nothing to be desired in point of accuracy. It is the apparent, not the real, specific gravity which is thus determined, unless indeed special measures be taken to expel enclosed air before weighing in water. Determinations are carried out as follows :—

A piece of the material, preferably of not less than 5 gr., is weighed by itself. It is then speared on a small brass skewer attached to one end of a suitable length of horsehair or very fine wire, the other end of which is tied to a small hook. Both the hook and the skewer are easily improvised from ordinary domestic pins. The object is then taken in a pair of tongs, immersed in a beaker of water, and cleared of the numerous air-bells which are sure to cling to it by brushing all over with a camel's hair or fine bristle pencil ; this operation should be conducted in a good light. The beaker is placed on a wooden support straddling over the pan of the balance ; the object is suspended from the hook above, and its weight under water is determined. The tare of the horsehair and hook, with the skewer immersed to a similar depth in water, must also be known. We have then weight in air, plus tare, minus gross weight in water as representing the weight of water displaced by the object, *i.e.* its volume ; from this and the weight in air of the object we deduce its specific gravity. Temperature correction—which, however, affects only the third place of decimals—is made by multiplying the specific gravity so found by the density of water at the temperature of experiment.

Materials lighter than water are dealt with in the same way, except that the object must be weighted with a sinker. This may consist of a smooth piece of metal to

which a looped pin-point is soldered, or which is slung from the object by a thread, or, yet more simply, of a piece of lead wire wrapped round the object. Needless to say, the tare of the sinker under water must be known and added to that of the suspension.

Rubber in small fragments or dust must be treated like a powder, *i.e.*, by pycnometry. For vulcanized rubber generally, hydrostatic weighing is to be recommended wherever practicable, as being less troublesome than the pycnometric method and more trustworthy than any flotation method, however ingenious or fascinating. In solids cooled from fusion without crystallizing, and in properly made rubber goods not purposely intended to be porous, true and apparent specific gravities may be accepted as identical. Unvulcanized rubber in crape form is quite amenable to the hydrostatic weighing method, provided it be boiled out *in vacuo* with especial thoroughness; if in lump form it should first be rolled into thin sheet or cut into narrow strips.

The specific gravity of pure resin-free rubber ranges from 0·91 to 0·96, largely according to botanical origin. Variations within the third place of decimals may depend upon crop, age of trees, mechanical treatment, &c. Plasticizing on the hot rollers generally raises the specific gravity about 0·005. Resin in any considerable proportion tends to raise the specific gravity, since the resins themselves are nearly as heavy as water, or slightly heavier. The rubbers from *Hevea*, *Castilloa*, and *Ficus*, whether wild or plantation, have a specific gravity of 0·91 to 0·92. *Manihot* rubbers are invariably somewhat heavier and show a greater range, viz., 0·93 to 0·96. The deresinified rubber of African sorts is equally heavy, seldom showing less than 0·93 but not often more than 0·95; in presence

of their resin, however, the more highly resinous sorts may reach as high a specific gravity as 0·98.

Vulcanization involves a condensation of matter, hence the specific gravity of vulcanized rubbers is always greater than that of the uncured doughs. Starting from a mixture of rubber with nothing but sulphur, this shrinkage is only 0·007—0·013 at soft cures (2°—4°), but amounts to 0·05—0·07 for ebonites (20°—50°).

Diluents and charge being absent, soft-vulcanized rubbers are still, for the most part, lighter than water, but ebonites are invariably heavier. The specific gravity of vulcanized rubber goods containing auxiliary materials, as determined by hydrostatic weighing, may be calculated additively from the components, assuming always that there are no vacuoles in the rubber. A quality made up of a parts of vulcanized rubber, sp. gr. A, b parts of a filler, sp. gr. B, c of another filler, sp. gr. C, and so on, will have the specific gravity

$$\frac{a + b + c + \dots}{\bar{A} + \bar{B} + \bar{C} + \dots}$$

Goods ordinarily met with in trade may thus have specific gravities ranging from less than unity to upwards of 2. In the old days before the rise of rubber chemistry, specific gravity was almost the only criterion of the quality of rubber goods which could be expressed in figures, and now as then experienced practical men can draw astonishingly far-reaching conclusions from inspection combined with a knowledge of the specific gravity. Apart from this, specific gravity is of no small direct importance in the manufacture of rubber goods. Most such are made up to definite limits of specific gravity, either to meet

peculiarities of popular demand, or to fit in with requirements as to weight in composite structures containing rubber, or because the goods are sold by weight, or for other reasons. Especially important is the distinction between floating (*i.e.* lighter than water) and non-floating

Filler.	Sp. Gr.	<i>n</i>	Sp. Gr. of Rubber.
Litharge	9·4	5	1·006
		10	1·043
		30	1·194
Zinc White	5·5	30	1·173
		100	1·590
Barytes	4·5	30	1·161
		100	1·541
Lithopone Antimony Red (not plastered)	4·1	10 30 100	1·031 1·154 1·519
Zinc Sulphide Magnesia Antimony Red (plastered)	3·3	5 10 30 100	0·997 1·027 1·139 1·456
Talc Whiting	2·7	30 100	1·120 1·390
Magnesium Carbonate Graphite	2·2	10 30	1·013 1·099
Lampblack	1·8	10 30	1·004 1·072

goods. Air-chambers of tyres, rubber strip and bands, golf-balls, certain kinds of sheet and tubing, and a host of minor articles, are commonly demanded in floating quality. The admixtures introduced into such goods must be regulated accordingly. Thus, starting from Para

rubber vulcanized with 10 per cent. of sulphur (sp. gr. 0·968), the floating limit is reached with about 9 per cent. of lampblack, 5—7 of antimony red, and only 4 of zinc white or litharge. On the other hand, no limit is set by waxes, oils, floating factice, or, within practicable proportions, bitumen.

The table on p. 108 shows the specific gravities of vulcanized rubbers made up of 100 parts of Para, 10 parts of sulphur, and n parts of some of the commonest pulverulent fillers.

In order to ascertain the true specific gravity of rubber goods which are blown or spongy, the pycnometric method must be resorted to, the sample having previously been ground fine on the rollers. Rubbers which cannot be reduced to crumb are cut by hand into the finest possible shreds. Thorough boiling out *in vacuo* is essential. In works practice it is often expedient to control internal blowing in vulcanized rubber goods, both qualitatively and quantitatively, by comparing the true with the apparent specific gravity of the goods.

CHAPTER VII

ANALYSIS OF MANUFACTURED RUBBER : ORGANIC

MOST people have at one time or another seen a pneumatic inner tube, a rubber heel, and an ebonite pipe-stem ; and there is no need to insist on the vast diversity in character of manufactured rubber articles. Nevertheless, essentially the same system of quantitative analysis applies throughout. Analysis may have for its aim (1) the detection or quantitative control of specified constituents, *e.g.*, ash, total acetone extract, free sulphur, total sulphur, alcoholic potash extract, etc., or (2) the elucidation, item by item, of the mixing from which the article was made. In the former case all is tolerably plain sailing ; but the complete proximate analysis of rubber goods, though there is nothing particularly arduous or esoteric about the analytical procedure, involves difficulties of interpretation which are hardly ever absent and are sometimes insuperable.

Heat-cured rubber goods are made by compounding rubber, sulphur, diluents, and charge, and vulcanizing the mixture to a low (soft rubber goods) or a high degree (ebonites). After vulcanization, they preserve their con-

stituents practically unaltered, except that part of the sulphur has gone into combination with the rubber and possibly also, though to an inconsiderable extent, with the charge. *Cold-cured* goods form a minor class confined to thin sheet, tape, or thread, thin-walled tubing, waterproofed fabrics, etc.; they are compounded without sulphur and are superficially vulcanized by means of sulphur chloride. No chemical changes in the charge, provided it be properly selected, are brought about by cold-curing, but the rubber goes into combination with both sulphur and chlorine.

Insertions and other inhomogeneities apart, the qualitative composition of manufactured rubber is summed up by the following scheme :—

Article.	Necessary Constituents.	Possible Constituents.
Heat-cured goods and Ebonites.	Rubber proper. Rubber-Resin and -Ash. Sulphur combined with rubber.	Free Sulphur.
Cold-cured Goods.	Rubber proper. Rubber-Resin and -Ash. Sulphur combined with rubber. Chlorine combined with rubber.	Diluents :— Waxes. Oils. Foreign Resins. Factice. Bitumen, &c.
Doughs and Solutions.	Rubber proper. Rubber-Resin and -Ash. If intended for vulcanization :— Free Sulphur. In the case of solutions :— Naphtha or other solvent.	Charge :— Inorganic Powders. Carbon Black. Fibres. Organic Dust.

The primary operations in rubber analysis are concerned with separating and isolating the above-named main classes of constituents. As regards diluents (and free sulphur), this is effected by extraction with a sequence of solvents. The charge, as a whole, is isolated by removing, and incidentally decomposing, all the organic components, and may then be subjected to further analysis. Rubber proper, once combined with sulphur or chlorine, cannot be isolated unchanged and is determined by difference or, in the rare cases where that is possible, by the bromine method. The sulphur and chlorine combined with rubber can be determined by special assays.

Before being subjected to analysis, rubber goods must be suitably comminuted. Certain classes of goods, viz., ebonites and highly charged rubbers, are readily reduced to coarse powder by the aid of a rasp. Most soft rubbers, however, cannot thus be dealt with. Whenever factice is known to be absent or does not need to be determined, it is quite satisfactory to cut up the rubber with a pair of scissors into snippets approximating to 2 mm. cubes. Where a set of mixing rollers is available, there is no better way of comminuting rubber goods than by "crumbing" them on the closely-set cold rollers. Goods rather highly vulcanized or containing much charge can thus be brought into the state of a woolly mass or even of a powder. High-class elastic rubbers, on the other hand, cannot be fully disintegrated, but go into the form of crape. If this crape be thin enough, it need only be cut up with scissors and is then suitable for any analytical operation. A certain amount of heating inevitably takes place when rubber is sent through the rollers, but great care must be taken that it does not go too far. As a substitute for orthodox rollers, the small metallurgical

mill mentioned on p. 26 (Fig. 9) may be made to do good service.

Manufactured articles made from a single mixing are usually homogeneous enough to render averaging of samples unnecessary. Parti-coloured goods, however, will have to be averaged from a fairly large bulk if they are to be analysed as a whole. In dealing with composite rubber goods, *e.g.* tyres, cable-coverings, etc., it will generally be desirable to analyse each section or layer separately; since these cannot, given a well-made article, be separated by stripping, there is nothing for it but to cut out the various samples as cleanly as may be with the aid of a sharp wet knife and a pair of scissors. Rubber laid upon fabric can similarly, if thick enough, be shaved off with a wet knife. When the fabric is rubbered on one side only, it can often be stripped away after wetting with steam or boiling water. Another artifice, which, however, involves slight losses of extractive matter, consists in soaking the rubbered fabric in naphtha and shaving off the swelled rubber, which is then dried until free from solvent. In the case of rubbers consisting of a single mixing and spread upon fabric in a thin layer, trouble may often be saved by analysing rubber and fabric together, due allowance being eventually made for the latter. In order to ascertain the relative proportions of fabric and rubber, the fabric is isolated in a clean or nearly clean condition by boiling in petroleum (see p. 141) followed by copious washing with naphtha; any rubber-fillers remaining entangled with the fabric may be determined and isolated by incineration.

I. Moisture.

Manufactured rubber may in general be assumed to be free from moisture. Rubber which has from accidental or extraneous causes become wet may be dried *in vacuo* or in an air-oven at 60°.

II. Acetone Extraction.

The first operation in rubber analysis, which is to be applied in all cases without exception, consists in extraction with boiling acetone. One or two gr. of material are placed in a filter-thimble, covered (if in the state of powder) with a plug of fat-free cotton wool, and extracted in a Knöfler tube for ten hours. In the case of ebonites it is safer to extract for twenty hours. Acetone which has stood for a long time may contain terpenoid bodies and must be redistilled before use. During extraction, note should be taken whether yellowish matter is being dissolved out slowly and hesitatingly; if in that event the extracts are barely fluorescent, bitumen is indicated; if strongly fluorescent, coal-tar pitch. A nearly colourless fluorescent extract points to mineral oil. Before being distilled, the extract is allowed to cool completely, and any deposition which may take place is observed. Sometimes free sulphur crystallises out in long monoclinic prisms. A bulky translucent crystalline growth will be due to paraffin or ceresine. Oily drops will in most cases consist of factice-extract. All these substances dissolve easily in hot, sparingly in cold, acetone; hence the necessity of extracting with boiling solvent. When determinations other than that of free sulphur have eventually to be made in the extract, two or more separate extractions of the same rubber must be carried out.

The extract, in its 100 c.c. or 150 c.c. Soxhlet flask, is distilled from a water-bath, dried, and weighed. Free sulphur, if present, is apt to give trouble by causing violent spitting in the later stages of distillation; when spitting sets in, it is advisable to stop the distillation, to add a little benzene or carbon disulphide, and to continue evaporating with or without condensation. The flask is dried, to avoid loss of sulphur, for not more than one hour at 110° or for three hours at 60°; but if there is a large amount of extract, say over $\frac{1}{2}$ gr., it is well to prolong these periods.

Substances completely extracted by acetone:—

- Free Sulphur
- Rubber-resin and other resins
- Oils, mineral and fatty
- Paraffin and ceresine.

Acetone extracts may in addition contain the acetone-soluble matter accompanying

- Factice
- Reclaim
- Bitumens and pitches.

Free Sulphur is, of all rubber components, the one most liable to uneven distribution. After vulcanization, the sulphur left uncombined is evenly distributed throughout the mass in a colloidal or other metastable condition. Sooner or later, however, and to a greater or less extent, it tends to work to the surface and there ultimately to assume the stable crystalline (rhombic) form; this constitutes the familiar phenomenon of "sulphuring up." Some judgment, therefore, is necessary in sampling goods which have visibly sulphured up. It should also be borne in mind that goods which have undergone super-

ficial wear will have lost that portion of their free sulphur which has thus effloresced.

Free sulphur in acetone extracts is determined by one of the following methods :—

1. *Differential Solubility Method*, by which sulphur is isolated and weighed as such. To the extract in its flask are added 20 c.c. of petroleum spirit (B.P. 60°—100°) saturated in the cold with sulphur. After shaking and standing, the resin, etc., is dissolved out and the sulphur left behind. The clear liquid is separated and the residue washed two or three times with fresh reagent, and finally with pure solvent free from sulphur. If the residual sulphur is well crystallized, these operations can be effected by simple decantation ; if not, it will be necessary to pass the liquids through a filter and collect the retained sulphur by the aid of carbon disulphide. Finally the sulphur is dried in the original flask at 60° and weighed. The success of this method depends on whether all the non-sulphurs go readily into solution, and from this point of view petroleum spirit is a much better solvent than acetone itself, which in the cold does not easily take up waxes, factice-extracts, and bitumen-extracts, whereas petroleum spirit does. The solubility of sulphur in cold petroleum spirit is trifling, viz. about 3 gr. per litre. Paraffin in considerable quantity may give trouble in refusing to dissolve, as also the extracts from coal-tar and other pitches and those from the fancy resins sometimes occurring in ebonite. Though inapplicable in these exceptional cases, the method is in general accurate enough for most practical purposes.

2. *Thiocyanate Method*, based on that of C. Davis and J. L. Foucar.¹ The extract is boiled under reflux with

¹ *Journ. Soc. Chem. Ind.* **31** (1912), p. 100.

25 c.c. of ordinary (95 per cent.) alcohol and about 1 gr. of potassium cyanide in lump form, during half an hour, or longer if there be much sulphur. What remains of the cyanide is fished out, and the alcohol is driven off by distillation. The sulphur has now been converted into potassium thiocyanate. About 50 c.c. of water, a slight excess of nitric acid, and some iron alum are added. Titration is then carried out with $N/10$ or $N/5$ silver nitrate solution to disappearance of the red colour. The last-named operations should be conducted in the draught-cupboard. One gr. Ag = 0.297 gr. S.

3. *Oxidation Method.*—To the extract are added 2—5 c.c. of sulphur-free nitric acid and a pinch of powdered potassium chlorate. The flask is covered with a watch-glass and warmed on a water-bath for about six hours. If much sulphur be present, it may be necessary to add more chlorate from time to time; care should be taken not to let the sulphur melt. When all the sulphur has been oxidized, the liquid is diluted with much water containing a few c.c. of hydrochloric acid, filtered cold, and precipitated with barium chloride. The method is more especially useful when quite small amounts of sulphur have to be determined with accuracy.

Mineral Oil, Vaseline, Paraffin, etc.—These hydrocarbons may be isolated by destroying the rest of the extract by means of sulphuric acid, the method being adapted from one which has long been in use for the assay of ceresine in crude ozokerite. When isolated, the hydrocarbons, whether oil, vaseline, or wax, can usually be identified by their appearance and consistency. To the extract are added $1\frac{1}{2}$ —2 c.c. of concentrated sulphuric acid, and the flask, covered with a watch-glass, is heated in an oven at 110° for 3—4 hours. The right

dose of acid varies with the amount of resin to be decomposed, and should be so regulated that the final magma flows with difficulty. Thirty c.c. of petroleum ether (B.P. 40°—60°) are then poured in and boiled under reflux for an hour. The solution is decanted into a separating funnel and the flask is rinsed out with solvent, transference of acid being carefully avoided. The petroleum ether solution is now thoroughly washed with caustic soda solution (10—20 per cent.) to which half its volume of alcohol has been added. Finally the solution is evaporated in a tared flask, which is then dried for 2—3 hours at 110° and weighed. The method fails when very large excesses of resin are present, but is otherwise quite satisfactory, with perhaps a slight tendency to high results. Mineral oils and waxes in acetone extracts, it may be observed, sometimes originate not as direct compounding materials but as factice-ingredients (see p. 41). A portion of the extract from bitumens, also, is of the nature of hydrocarbons resistant to sulphuric acid.

Paraffin and Ceresine.—No analytical distinction between these two waxes can advantageously be made (but see p. 96). When the wax is isolated, there is often no difficulty in recognizing the one or the other by its consistency. An old-established method of determining solid hydrocarbons, when these alone are present, rests on the principle of differential solubility and may be carried out as follows:—

The extract is boiled under reflux with 30 c.c. of alcohol, which should be as nearly as possible of 97 per cent. strength (*e.g.*, about equal volumes of absolute and ordinary alcohols). If globules of molten substance remain undissolved, more alcohol must be added. The solution is decanted from any solid residue and cooled

under running water. Ice-cooling is a refinement which adds but little to the accuracy, such as it is, of the assay. The waxy matter which crystallizes out is received on a filter, washed with alcohol (90 per cent.), and rinsed with the same into a tared Soxhlet flask. After removal of the liquid by evaporation, the residue is dried and weighed as usual. A slight plus correction may be made on account of the paraffin remaining dissolved in the mother-liquor. The conditions of solubility of hard paraffin in alcohol are approximately these :—

Alcohol.	Solubility at boiling-point.	Solubility at 18°.
100 per cent.	4·0 gr. per 100 c.c.	0·20 gr. per 100 c.c.
97 "	1·6 "	0·11 "
96 "	0·7 "	0·08 "
95 "	0·3 "	0·04 "

It follows from these data that to dissolve 0·2 gr. of paraffin (more than this is not likely to occur in an acetone extract), 30 c.c. of boiling 97 per cent. alcohol should suffice, and that 0·033 gr. of paraffin will then escape into the mother-liquor. Against the latter item is to be set the sulphur which, provided that free sulphur be present in appreciable quantity, will find its way into the deposited paraffin and call for a slight minus correction. This sulphur, which may be anything up to 5 per cent. of the wax, can be determined in the weighed paraffin by the thiocyanate or nitric acid method.

Other Components of the acetone extract present unsolved analytical problems, so far as generally applicable methods are concerned. *Rubber-Resin* itself is so variable

a substance that there is no means of determining it directly. *Fatty Oils*, again, cannot be estimated in presence of rubber-resin by the simple process of taking the saponification number, because some resins (from Para and plantation sorts, especially) have a high saponification number of their own, whilst others (from African sorts, especially) have next to none. The same argument applies to *Factice-Extract*, with the added complication that this class of body itself shows a considerable range of saponification numbers. No direct method for the determination of *Bitumen-Extract* is as yet known. When either of the two last-named is present, an approximate estimation can be made on the basis of the figures subsequently found for factice and bitumen insoluble in acetone. In the case of factice, the assumption may be made that roughly 10 per cent. of white or 20 per cent. of brown factice are acetone-soluble and go into the present extract. As for bitumen, the estimation of extract on these lines is even more uncertain, seeing that anything between 50 and 80 per cent. of the total bitumen may be dissolved out during acetone extraction; but 70 per cent. may be regarded as a rough average (see p. 54).

Rubber-Resin.—In the simplest cases, which embrace most of the better-class rubbers, acetone extract consists of rubber-resin plus free sulphur, plus, possibly, mineral wax. Sulphur can be determined accurately, mineral wax with tolerable accuracy; hence rubber-resin can be estimated by difference with no great error. The importance of this lies in the fact that by calculating it as a percentage of resin plus rubber proper (as subsequently determined), the resin-content of the raw rubber or rubbers originally employed is arrived at. The

original resin-content is not affected by vulcanization, except in so far as a small part of it is rendered insoluble in acetone ; the more, the higher the vulcanization. This insolubilized portion may amount to several per cent. in ebonites, where it eventuates in the alcoholic potash extract ; in soft rubbers, however, it is so small as to be practically negligible. Original resin-content, thus ascertained, often gives useful information for identifying the raw rubber sort, at any rate within limits. Occasionally also rubber-resins possessing characteristic odours (Para, Guayule, certain Africans, etc.), can be recognized in the acetone extract. The polariscopic test (p. 16) effects little more than a classification into rubbers poor and rich respectively in resin. There is, in fact, no certain way of identifying original rubber, either through the rubber itself or through its resin. The best one can hope for is an indication pointing to this or that class of rubber, which, to an experienced rubber analyst, may often be of considerable value.

When factice or bitumen is present in even small amount, the estimation of rubber resin by difference is attended with some uncertainty. To allow for factice-extract, the best plan is to regard 10 per cent. of the factice subsequently extracted by alcoholic potash, if white, or 25 per cent. if brown, as belonging to the acetone extract. With bitumen the uncertainties are even greater. Roughly speaking, the acetone extract is about five times the carbon disulphide extract subsequently determined (see p. 54). In inferior rubbers containing large admixtures of these diluents, conventional ratios between matter soluble and insoluble in acetone are no longer to be trusted as aids to estimating rubber-resin by difference. When reclaim is present, all ordinary calcula-

tions are upset, and each case must be judged, as shrewdly as may be, on its merits.

III. Carbon Disulphide Extraction.

This operation concerns bitumens and pitches only. To ascertain whether there is any need for it, a sample of the original or acetone-extracted material is covered in a test-tube with carbon disulphide; the formation of a decidedly brown solution indicates presence of bitumen or pitch. A qualitative distinction between these two may be made by means of pyridine, which has no effect on bitumen but readily dissolves coal-tar pitch, yielding reddish solutions with a strong green fluorescence. In general, the presence of bitumen or pitch will already have been remarked in the course of acetone extraction (see p. 114). Formerly it was a safe rule that these diluents could occur only in black or grey rubbers; nowadays, however, bitumen of the "mineral rubber" type is sometimes to be found, in very small proportion, in reds and whites.

The residue from acetone extraction, in its filter-thimble, is dried in the open air or by being put for about a quarter of an hour in the oven. It is then plugged with cotton wool (this is indispensable owing to the high specific gravity of the solvent) and extracted in a Soxhlet or Knöfler tube with fresh carbon disulphide. Usually a few hours suffice, but in presence of a large proportion of bitumen it may be necessary to extract for ten hours or longer. The operation is at an end when the liquid surrounding the thimble remains quite colourless after standing for half an hour. The extract is distilled, dried for 1—3 hours at 110°, and weighed. Carbon disulphide will dissolve out no rubber, unless the material be under-cured. To meet

this eventuality, the dried extract is treated repeatedly with cold carbon disulphide in small doses until no more coloured matter goes into solution. If a pellicle of rubber is now left behind, it is dried and weighed, and its weight is subtracted from that of the total extract.

It should be borne in mind that the bitumen thus found represents quite a small fraction (10 to 30 per cent., according to circumstances) of the bitumen originally added to the rubber. More than half of the total bitumen will have been already removed by acetone. On the other hand, a certain proportion, of the same order of magnitude as the carbon disulphide extract itself, resists solvents altogether and passes on into the final residue of vulcanized rubber. Some data as to the distribution of bitumen which, if used with caution, may serve as the basis of calculations for the present case, are given on pp. 54—55.

IV. Alcoholic Potash Extraction.

The next and last process of extraction consists in the removal of factice, or rather of the essential, fully vulcanized, constituent of factice. This is effected by saponification, whereby the factice is converted into glycerine and alkali-soaps soluble in alcohol. Too much stress cannot be laid on the necessity of having a finely-divided sample, procured either by rasping or crumbing, for this determination. Alcoholic potash penetrates rubber with such difficulty that it may very well extract only a fifth or a tenth of the factice actually present, if the rubber be merely cut up into snippets.

The rubber left over from the previous extractions is spread on a dish, freed from solvent by air-drying, and transferred to a 100 c.c. flask ground-in to a reflux condenser. The apparatus designed for the toluene extraction

of gutta-percha (Fig. 22*b*) serves equally well for the present purpose. Fifty c.c. of *N/5* alcoholic potash, or 10 c.c. of *N/1* suitably diluted with alcohol, are added, and the mixture is boiled on a sand- or water-bath for three hours. The reagent employed should not be dark in colour, but yellow at most; it should be made up with clean spirits of wine (not methylated spirit) and kept in a well-lighted place. In taking up factice, it assumes a more or less deep brown colour.

The liquid is poured away from the rubber and distilled nearly to dryness from a water-bath. Meanwhile the rubber is boiled up with three relays of 20 c.c. of water and wrung out, the combined washings being added to the distillation-residue. The clear soap-solution thus obtained is transferred, when cool, to a separating funnel, acidified with hydrochloric acid, and extracted two or three times with ether. The ethereal extract is distilled in a tared Soxhlet flask, dried for an hour or two at 110°, and weighed.

The brown evil-smelling mass thus obtained consists not of factice but of factice-acids, and requires a small plus correction. On the average, the yield of acid from acetone-extracted brown factice is 94 per cent., from white factice 88 per cent. In order, then, to arrive at the weight of unsaponified factice, the weight of factice-acids is multiplied by 1.136 if chlorine (indicating white factice) is found in the alcoholic potash extract, or by 1.064 if chlorine is absent. The older method of factice-determination, by which the rubber was weighed before and after extraction, is open to more than one serious objection and is not to be recommended.

It is often desirable to determine the sulphur of vulcanization combined with the extracted factice. To

this end a separate extraction must be made, because a certain amount of sulphur (and most of the chlorine) is split off in the operations described above. A separate alcoholic potash extract, accordingly, is evaporated in an iron bowl, and the sulphur is determined by the potash-peroxide fusion method (see p. 43). So also both sulphur and chlorine may be determined in the same extract, but there is little to be gained from chlorine determinations unless the simultaneous presence of white and brown factice be suspected, since white factices do not vary notably in sulphur- and chlorine-content (*cf.* p. 45).

The percentage of factice determined by means of alcoholic potash falls short of the factice originally present by so much as has already been dissolved out by acetone. In calculating back to mixings, then, the factice now found should be increased by one-fourth in order to arrive at original brown factice, and the same quantity should be subtracted from the acetone extract of the rubber. In the case of white factice the allowance will be one-ninth of the factice found.

V. Combined Sulphur.

After these various extractions, what we have left is rubber hydrocarbon, plus the sulphur of vulcanization combined with it, plus the charge. Before going on to the analytical treatment of charge, it will here be well to consider the determination of combined sulphur. In the majority of heat-cured soft rubber goods the sulphur of vulcanization ranges between 2 and 4 per cent. of the rubber proper, and when it is desired merely to obtain approximate information as to the original mixing, it does well enough to assume that for 100 parts of rubber hydrocarbon there are 3 parts of combined sulphur.

present. This sulphur, added to the free sulphur previously found, gives total sulphur as compounded in the mixing.

From another point of view, however, sulphur of vulcanization calls not only for direct determination, but for accurate determination. The *coefficient of vulcanization* of any rubber, which may more briefly be denominated *degree of sulphur* and be expressed in degrees, is defined as the parts of rubber-combined sulphur present per 100 parts of pure sulphur-free rubber hydrocarbon. This quantity is very characteristic of the rubber and the cure. In any given mixing, it increases with the temperature of the cure, the duration of cure, and the proportion of sulphur incorporated; moreover, all these conditions remaining constant, it varies with the species of rubber employed. What is considered correct vulcanization for any given mixing can be, as it were, registered by means of the degree of sulphur. There is no need, therefore, to insist on the importance of determining sulphur of vulcanization in connexion with manufacturing practice.

The determination of degree of sulphur involves three distinct assays, viz. :—

- (a) That of total combined sulphur.
- (b) That of inorganically combined sulphur, if present.
- (c) That of rubber hydrocarbon.

All these being expressed as percentages of original material, we have

$$S = \frac{100(a - b)}{c} \text{ degrees.}$$

Assay (b) is carried out on a portion of the isolated charge (see p. 141). Rubber proper is usually estimated by difference (see p. 132) and in complicated mixtures is liable to come out with an error of several per cent.

In order not to aggravate this error, it is well to determine sulphur as accurately as possible. The percentage of combined sulphur in high-class soft rubbers ought to be stated correctly within \pm 3 to 4 units in the second place of decimals. In highly charged goods a somewhat wider limit of error must be allowed. With ebonites, which may be cured up to 40° or higher, the second place of decimals may be disregarded.

Total combined sulphur in rubber goods is determined in the residue remaining after all the extractive operations have been brought to an end. If it be intended to weigh out a portion only of the residue in hand, this residue must previously be completely dried and then weighed. Extracted rubber has a peculiar tendency to take up oxygen, so that the drying must be done with care. The best thing is to heat in the air-oven at 110° until the water or organic solvent is nearly expelled, and to finish in the vacuum-oven. Generally speaking, however, it makes for accuracy to weigh out a separate sample of original substance, to subject it to the various extractions, and to use it bodily, after cursory drying, for the determination of combined sulphur.

Of the various methods available, two may be specially recommended. By the classical method of Henriques, now over thirty years old, the rubber is nitrated and the organic matter then destroyed by fusion with alkaline nitrate. Very accurate results are obtained, but the method is tedious and much at the mercy of accidents, and is useful rather as a check method than for routine work. The second method, in which sodium peroxide is the oxidizing medium, dates from the comparatively recent time when that reagent became cheap and familiar. It has for some years past been extensively practised in

numerous modifications, amongst which the one described below is as rapid, accurate, and handy as any.

The amount of material to be weighed out should be 1 gr. of high-class (especially floating) qualities, 0·5 gr. of heavily charged qualities, or 0·3 gr. of ebonite.

1. *Nitrate Fusion Method.*—The rubber is placed together with 15 c.c. of sulphur-free concentrated nitric acid in a 25 c.c. porcelain crucible of the wide-mouthed type, which is covered with a watch-glass and warmed, cautiously at first, on a water-bath. When the evolution of nitrous gases has ceased, the watch-glass is removed and the mixture is evaporated. Should fragments of rubber remain undecomposed, evaporation with more nitric acid will be necessary. The contents of the crucible now consist of a yellow slime, to which carbon black or bitumen, if present, may impart a black discolouration. Whilst the sticky mass is still warm, 5 gr. of a finely-powdered mixture of sodium carbonate and potassium nitrate (5 : 3), both sulphur-free, are added in small portions at a time and uniformly incorporated with the aid of a thick iron wire hammered flat at the end. The crucible and its contents are then dried in the air-oven; practised analysts, however, will combine this with the next operation, taking care that condensed moisture is not allowed to remain on the crucible-cover. The mixture (which, it will be noted, is nothing more or less than a kind of slow gunpowder) is now very cautiously heated over a small flame until reaction sets in, when the flame is at once withdrawn. The crucible meanwhile is covered with its lid, or with a semi-flat porcelain dish, bottom downward; in case solid particles are thrown on to the cover, they can subsequently be scraped off and added to bulk. Reaction should take the form of a

slow and mild deflagration with evolution of bluish smoke. Provided the reagents be finely powdered and intimately mixed, and not heated too quickly, there is no risk of anything so violent as an explosion. Reaction over, the flame is urged and the contents of the crucible are brought to fusion and well stirred with the iron wire previously used. After remaining in fusion for a short time, as much as possible of the melt is poured and scraped on to an iron plate and then thrown, whilst still hot, into a beaker of water. The cooled crucible also is digested with hot water. When the melt has been completely lixiviated, the liquid is filtered. The residue, which contains *inter alia* carbonates of all the lead, zinc, barium, calcium, and magnesium present in the rubber, is worth preserving in case check determinations of these metals should be required. The filtrate is strongly acidified with hydrochloric acid, evaporated to dryness, taken up with water, and filtered; whereupon precipitation by means of barium chloride is effected in the usual way.

2. *Potash-Peroxide Fusion Method*.—The most convenient vessels for this fusion are hemispherical bowls of spun sheet-iron, about 10 cm. diameter, such as are commonly used for sand- or oil-baths. They are cheap, and last out twenty or thirty fusions. Large nickel crucibles serve equally well, but are both dearer and less durable. The rubber is placed in a bowl with 16 gr. (usually corresponding to 16 cm.) of stick potash or less, according to the amount of rubber proper present, and 2 c.c. of water; more water than this is both superfluous and undesirable. The potash is dissolved by gentle heat and boiled down at a simmer. Now and afterwards the contents of the bowl should be kept well mixed, either by means of a

long iron spatula or by agitating the bowl held in a pair of crucible tongs. When the rubber begins to melt, the flame is so regulated that decomposition, accompanied by evolution of a bluish fume, takes place at a steady and not too rapid pace. After 15—20 minutes, volatile matter will cease to be given off and the melt will consist of a homogeneous dark mass. The spluttering which continues up to this point does not seriously affect the accuracy of the assay, but is very disagreeable to the operator, who will do well to wear gloves. A lid of sheet iron may be used, but the process is less well under control, especially as regards keeping the melt properly mixed. Sodium peroxide is now added in pinches, and thoroughly incorporated. The amount required varies between 2 and 5 gr. and may be gauged by the circumstance that when oxidation is complete the melt changes from a light green to a dark purple colour due to ferrates and permanganates. Should effervescence take place on adding the peroxide, it is a sign that the fusion with potash alone has not been urged far enough. Care must be taken that the oxidizing magma comes into contact with the whole inner superficies of the bowl.

After cooling, but whilst still warm, the bowl is three-quarters filled with water. The dissolved contents are rinsed into a beaker, made up to 400 c.c., treated with concentrated hydrochloric acid until the ferric oxide is just dissolved, further acidified with 5 c.c. of the same, and boiled. In the absence of barium the liquid will be perfectly clear, though strongly coloured by ferric chloride. Whether barium be already present or not, the boiling liquid is now precipitated with a decided excess of barium chloride and allowed to cool completely; this latter precaution is necessary, because barium sulphate is by no

means insoluble in the hot, acid, highly saline liquid. The precipitate is filtered off and weighed as usual. From beginning to end the whole assay can, if desired, be carried out within $2\frac{1}{2}$ hours. Should the stick potash contain sulphur, the requisite correction is determined once for all by a blank assay; but most of the better brands are practically free from sulphur.

This method (but not the preceding one) lends itself also to the determination of chlorine of vulcanization in cold-cured goods, precisely as in the case of white factice (see p. 44). If, however, the rubber has previously been extracted with alcoholic potash, the determination will have no quantitative value, since cold-cured rubber gives up most of its chlorine to alkali. With a cold-cured rubber containing white factice, the best course is to determine total chlorine immediately after acetone extraction and to deduct 8 parts of chlorine per 100 of factice separately determined by means of alcoholic potash.

Mineral Combined Sulphur.—By this is meant the total combined sulphur contained in the pulverulent constituents (charge) of the rubber, and it is determined directly in a portion of the charge isolated by the method described in the next chapter. As much as can be spared of the charge (previously well mixed) of black and grey rubber may be weighed out, but in the case of whites and reds not more than $\frac{1}{2}$ gr. should be taken. The powder is boiled down with 5 gr. of stick potash and oxidized with sodium peroxide as above; there being little or no organic matter to get rid of, the whole business is over in less than ten minutes. Or, still more simply, the powder is directly mixed with about 3 gr. of peroxide in a small iron or nickel crucible and heated to fusion; but if the powder contains a high proportion of sulphides or of carbon black,

it must be diluted with a little magnesia to mitigate the violence of the reaction. The melt is dealt with as before. Mineral sulphur thus found is calculated as a percentage of the original rubber and subtracted from total combined sulphur similarly calculated; this gives sulphur of vulcanization. Sulphur of vulcanization calculated as a percentage of rubber proper (itself a percentage of original material) constitutes the degree of sulphur.

When a rubber is to be examined for degree of sulphur only, one gramme is weighed out, extracted, and treated by the nitrate or potash-peroxide method. Another gramme (except when mineral ingredients are altogether absent) is dissolved as on p. 141, and the whole of the charge isolated from it is similarly treated. The result of the latter assay is simply subtracted from that of the former. This double operation is, or should be, a very frequent item of factory routine in cases where the percentage of rubber proper in the mixing is already known. In these cases, moreover, the separate determination of mineral sulphur can often be dispensed with; but it should be noted that it is a little unsafe to calculate mineral sulphur, if there be much of it, from the compounding materials as specified on paper, and that when lead compounds are present the actual determination of mineral sulphur in each sample is a matter of necessity.

VI. Determination of Rubber.

Although much work has been expended on the determination of rubber by direct methods, there can be no doubt that, as matters now stand, the only trustworthy general way of arriving at the percentage of rubber in vulcanized goods consists in simple estimation by difference. In former times, when inorganic matter could be

determined only by incineration, the difference method was liable to rather large errors, but the application of centrifugal machinery has altered all that. Rubber proper, then, is determined by adding up the percentages of the various extracts, total charge, and sulphur of vulcanization, and subtracting the sum from 100. As a rule, it is quite feasible thus to estimate the content of rubber proper within one or two per cent. of itself. When bitumen is present, a certain amount of vulcanized bitumen will remain with the rubber and evade direct determination; the best that can be done in such cases is to apply an approximate correction (see p. 54).

Vulcanized rubber combines with bromine as readily as unvulcanized; the presence of mineral fillers, however, militates against the accurate determination of rubber as tetrabromide, and the sulphur of vulcanization also introduces some uncertainty. When there is no mineral matter, or none except barytes, silicates, and carbon, rubber can be determined, after extraction, in both soft rubbers and ebonites by the tetrabromide method (see p. 14). Under the action of bromine, part of the combined sulphur is split off as sulphur bromide, whilst the remainder persists in the rubber bromide.¹ For soft-cured goods of 2°—4° of sulphur, the same factor of conversion, viz., 0·42, holds approximately good as for unvulcanized rubber. For ebonites the factor ranges between 0·6 and 1·0, according to the degree of vulcanization.

VII. Analysis of Unvulcanized Goods.

This is a minor branch of rubber manufacture, limited to certain special articles. Unvulcanized insulation-strip

¹ W. A. Caspari, *Le Caoutchouc et la Guttapercha*, 8 (1911), p. 5289.

is usually free from mineral charge, but may contain factice and waxy hydrocarbons. Among more or less highly charged doughs sold as such may be mentioned tyre-repairing compositions, in which much litharge or other accelerator may be expected; doughs for surgical and dental ebonites; bands or cords for sealing tins, &c. Exactly the same mode of analysis is applicable to all these as to vulcanized goods, from which they differ only in containing no rubber-combined sulphur. Certain modifications are, however, dictated by the fact that uncured dough is apt to melt and clog when slightly warmed, and so to resist extraction by boiling solvents. When the material is not already in the form of sheet or cord, it should be rolled into sheet of not more than 1 mm. thickness. This is cut into strip, weighed out, and wrapped spirally in stout gauze, whereupon it is ready for extraction with acetone and alcoholic potash. When the dough is available only in lump form, it is cut up as finely as possible, and the snippets, after being wrapped layer-wise in filter-paper or gauze, will yield their extractive matter readily enough to acetone—but not always quantitatively to alcoholic potash. The latter difficulty may be overcome by the following artifice:—the acetone-extracted material is swelled and dissolved in ten parts of benzene, and the magma is mixed with alcoholic potash solution (which precipitates the rubber in porous clots) and boiled as usual. The extract is transferred to a separating funnel and shaken with a few c.c. of water; the bulk of the benzene then separates out and is rejected. At least one more extraction of the rubber clot is carried out, and finally the united extracts are further treated as on p. 124.

Carbon disulphide extractions being impracticable in

the case of uncured dough, bitumen, if present, must be approximately estimated from the acetone extract. Failing this possibility, the best plan is to vulcanize a portion of the sample, *e.g.* by pressing into a test-tube and heating in an oil bath, and then to proceed as usual.

VIII.—Analysis of Rubber Solutions.

The rubber solutions current in trade and within factories range from dilute solutions containing 5—10 per cent. of rubber and little or no charge to thick pastes or cements in which there is much pulverulent filling and comparatively little solvent. The solvents in use are coal-tar hydrocarbons, petroleum hydrocarbons, carbon disulphide, and carbon tetrachloride, or mixtures of two or more of these. Rubber solutions may be analysed as follows :—

1. Fifty gr., or as much as can be spared, of solution are steam-distilled until the runnings are no longer turbid. The non-aqueous portion of the distillate is separated off and subjected to fractional distillation, specific gravity determination, and chemical tests. The nature of the solvent or solvents is thus ascertained.

2. Five to twenty gr., according to concentration, of well mixed solution are spread on a wide flat porcelain dish, which is covered with a clock-glass and weighed. The dish is dried in the vacuum oven, so that the dissolved matter forms a thin elastic film on the bottom of the dish. This film is drawn off and turned upside down, and drying is continued to constancy of weight. The loss in weight gives the percentage of solvent, which cannot be determined accurately by steam-distillation owing to the difficulty of expelling the last traces. The residual

film of rubber thus obtained is examined by the usual methods of rubber analysis.

In some solutions and pastes, especially those intended for cementing solid tyres, rubber is replaced wholly or partially by gutta-percha or balata. A quantitative separation of these hydrocarbons from rubber is impracticable, but information as to the presence of gutta can generally be obtained by isolating and examining the pure hydrocarbons; to this end, the solution is suitably diluted and centrifuged, and the clear liquid is precipitated with alcohol. As distinguished from indiarubber, gutta-percha and balata are more plastic and almost destitute of tensile elasticity, and they are much less viscous in solution.

IX.—Analysis of Ebonite.

Ebonite is the product obtained when rubber is mixed with 30—50 parts of sulphur and subjected to prolonged cure at high temperature. It not only has a high degree of sulphur but also contains rather large percentages of uncombined sulphur, which does not effloresce to the surface. Superior ebonites, especially those which take a high polish, are made with little or no filling matter; in the cheaper kinds, diluents and pulverulent ingredients play an important part, and the proportion of rubber may tail off to near vanishing-point.

In all essentials, the analysis of ebonite is conducted on the same lines as that of soft rubber. The material is easily comminuted by rasping. Acetone extraction should be continued for 20 hours. Alcoholic potash, even if no factice at all be present, will invariably extract a few per cent. of saponifiable matter which has been formed by the action of sulphur upon resin, etc. Mineral matter must be determined by ash-analysis (see p. 158),

antimony and mercury being separately determined, as also carbon.

A frequent ingredient of ebonite is *added resin*. So far as this consists of rosin or rubber-containing resins, it finds its way completely into the acetone extract. The hard varnish-maker's resins, however (copal, shellac, etc., etc.), are insoluble, or only partially soluble, in acetone. In order to obtain information as to the presence of these latter, the ebonite is subjected, immediately after acetone, to extraction with epichlorhydrin, B.P. 116°—117°. This is best done by boiling out the material in a flask under reflux condensation with two or three portions of solvent. From the united extracts the bulk of epichlorhydrin is removed by distillation from an oil-bath, and the remainder by adding one or two relays of clean alcohol to the residue and distilling off. *Casein*, which sometimes occurs as a filler, is easily detected by the soda-lime test for nitrogen and determined by a Kjeldahl assay; as factor of conversion of nitrogen to casein, 6·7 may be taken. *Cork Dust*, a not uncommon filler, is more insidious from the analyst's point of view. Taken alone, it yields 5—10 per cent. of extractive matter to boiling acetone and subsequently 40—50 per cent. to alcoholic potash. The fatty acids from the latter extraction form a brown, amorphous mass of firmer consistency than those from factice, and, unlike these, insoluble in cold petroleum spirit; in boiling petroleum spirit they are slightly soluble, a white subcrystalline deposit separating out on cooling. After extraction with alcoholic potash, cork dust still yields a little matter to dilute aqueous caustic lye; the red solutions so obtained give, on acidification, a light yellow precipitate almost insoluble in ether. By the aid of these data, cork dust in ebonite may be detected

and roughly determined, it being borne in mind that one or two per cent. of organic acids which are derived neither from factice nor from cork dust are always likely to be found in the alcoholic potash extract.

X. Reclaim and Ground Waste.

No general method has as yet been devised for determining reclaim or ground waste in vulcanized rubber goods, any more than for separating two or more raw rubber sorts, once vulcanized together. Even qualitatively it is by no means always possible to make sure of the presence of reclaim. In all cases, rubber analyses should be gone through in the normal way, regardless of its presence or absence; conclusions as to one or the other may afterwards be drawn from the analyses and from other tests.

The main chemical characteristic of reclaim in a vulcanized mixing is its comparatively high degree of sulphur. Whereas raw rubber in soft-cured goods is seldom vulcanized above 4° , reclams themselves show originally from 2° to 5° , and after re-vulcanization rise to a correspondingly higher degree. Hence from an abnormal degree of sulphur in a not obviously over-cured article the presence of reclaim may reasonably be suspected. A physical peculiarity of vulcanized reclaim is its relatively low capacity for absorbing solvents. In general, and with any kind of vulcanized rubber, tendency to swell in solvents decreases as the degree of sulphur rises; but as regards reclaim the purely physical condition of the material is an additional factor. Rubber goods made largely or wholly from reclaim, then, swell up much less when immersed in naphtha than those made from raw rubber. In goods containing both, a

curious pitted formation may often be observed when a perfectly plane surface is allowed to swell in naphtha. Another side of the same phenomenon is the circumstance that vulcanized reclaim is much less readily dissolved at high temperatures, *e.g.* by boiling petroleum (*cf.* p. 141) than ordinary vulcanized rubber. By its behaviour under this treatment, reclaim can frequently be detected with tolerable certainty, and it is conceivable that an approximate separation of raw rubber from reclaim in rubber goods, based on selective decomposition with solvents at different temperatures, may some day be worked out.

Little, if any, evidence of the presence of reclaim is to be gained from the accompanying non-rubbers. When, however, there is found an unexpectedly large variety of mineral fillers, some of them in quite small quantity, the presence of reclaim may well be suspected, since the tendency in compounding raw rubber mixings is rather to simplify than to complicate the charge.

The mechanical properties of rubber goods are of course affected to a considerable extent by the presence of reclaim, which can often be detected by merely fingering and inspecting the sample. Tensile strength and, still more, elongation at rupture, are much reduced. So, above all, is resiliency: the material feels more or less "dead" when pulled or bent, and recovery from deformation takes place sluggishly. At the same time, these effects may be just as well produced by inferior raw rubbers, or excess of foreign materials, or faulty cure; so that conclusions must be drawn with caution.

CHAPTER VIII

ANALYSIS OF MANUFACTURED RUBBER : INORGANIC

HAVING dealt with rubber diluents and sulphur, we now come to what is in the main a branch of inorganic analysis, viz., examination of the solid compounding materials ; and the first task will be to determine their aggregate percentage in the rubber. Until recent times there was no way of doing this save by incineration, which involves numerous inaccuracies, gives no information as to organic pulverulent fillers, and, by disguising the mineral combined sulphur, renders the determination of degree of sulphur difficult, if not impossible. By now, however, methods by which the rubber is dissolved away and the residual charge collected have been gradually brought to perfection. Of the numerous solvents by which rubber can be destructively dissolved, the one earliest proposed, viz., petroleum, is on the whole the best. The chief obstacle to be surmounted has been rather the difficulty of collecting the charge, which is obtained in very fine suspension and, in most cases, resists all attempts at filtration. This problem has been satisfactorily solved by the application of centrifugal machinery.

I. Determination of Charge.

In presence of little or no free sulphur, it is immaterial whether the original rubber or such as has undergone extraction be taken; when the total sample available for analysis is scanty, the latter is obviously to be preferred. Preliminary extraction is advisable in presence of much free sulphur, in order that possible after-vulcanization during the hot petroleum treatment may be avoided. The rubber must in any case be as finely divided as possible. One or two grammes are weighed into a 50 c.c. Erlenmeyer flask, and covered with 10 c.c. of a petroleum fraction (distilled from ordinary lamp-oil) of B.P. 200° upwards. Soaking overnight in the cold greatly facilitates the subsequent operation, but is not absolutely necessary. The rubber is brought into solution by heating in a bath of oil or fusible metal to not much over the initial B.P. of the solvent, *i.e.*, the liquid

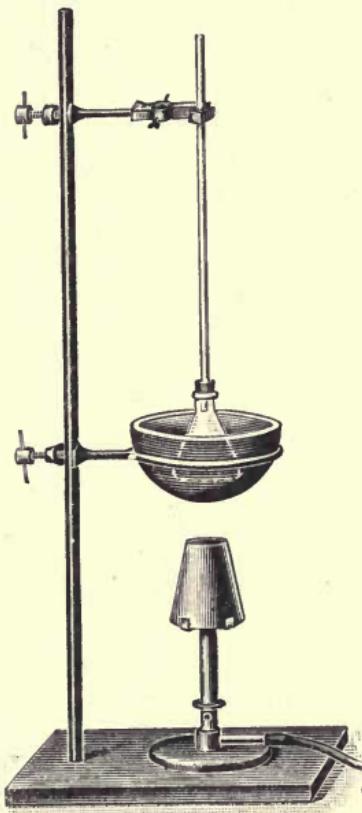


FIG. 18.

should be just on the simmer. A convenient disposition of apparatus is shown in fig. 18. The flask is held by a short stalk of glass tubing acting as reflux condenser, and is well shaken from time to time. Dissolution is completed in $\frac{1}{4}$ hr. to 2 hrs., according to

the degree of vulcanization; lightly vulcanized goods, especially if previously soaked, break up very rapidly. When the magma seems smooth and homogeneous it is cooled and settled, and the fluid portion is decanted off. Should undissolved lumps of rubber remain, more petroleum is added and heating is continued. Ultimately the whole magma is rinsed into a tared pear-shaped flask (see Fig. 12) with ordinary ether or light petroleum spirit, and is made up to about 50 c.c. Thick-walled cylinders of the Nessler-glass type, if not too heavy, are also quite suitable, but Erlenmeyer flasks should not be used in the centrifuge, as they can seldom be trusted to stand the strain. The flask or glass is counterpoised (to within 0·1 gr.) against a similar vessel holding the same kind of contents or merely water, and the two are whirled for 20–30 minutes in a centrifuge (see Figs. 10 and 11) running at 1500–2000 revolutions per minute. All solid matter, excepting negligible quantities which may remain in colloidal suspension, will now have gone to the bottom. If of a heavy and not too finely-divided character, the charge will often settle in so compact a mass that the supernatant liquid can be poured away to the last drop. As a rule, however, the liquid will have to be removed by siphoning, for which the apparatus shown in Fig. 19 may be used. The siphon, which should be of about 2 mm. bore, is started by sucking at *C*. Whilst at work the siphon is gradually lowered through the rubber joint *D* until it approaches the level of the solid deposit in *B* to within practicable limits. Eventually the volatile solvent is recovered by distillation from the receiver *A*. The charge is broken up with a wooden spatula, thoroughly shaken with 50 c.c. of fresh ether or petroleum spirit, and again whirled and separated. The same process is repeated

once or twice again, and the flask is then dried at 110° and weighed.

The feasibility of dissolving vulcanized rubber by means of hot petroleum reaches its limit at a degree of vulcanisation somewhere between 5° and 10° . On ebonite, hot petroleum has no dissolving action worth mentioning.

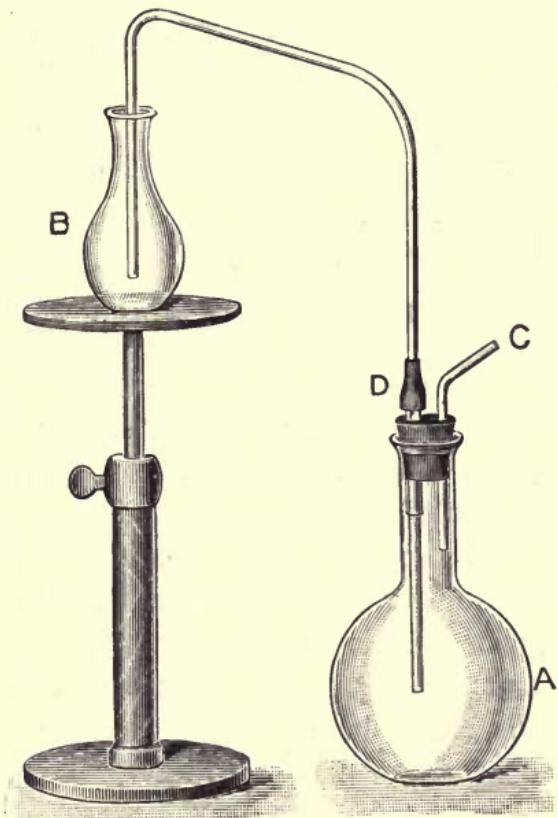


FIG. 19.

Since revulcanized waste and reclaim are apt to attain somewhat high degrees of sulphur, it often happens that rubbers containing these ingredients refuse to go completely into solution. The isolated charge will then be contaminated with rubber, and will come out too high. After the subsequent treatment of the charge with hot

acid, this impurity can sometimes be skimmed off, dried, and weighed; more usually it will have to be filtered off together with insoluble mineral matter and determined by ignition loss. Should a really important proportion of the original rubber remain undissolved in the form of flakes after petroleum treatment, the presence of ground waste or reclaim may safely be concluded; it is often worth while to isolate these flakes and examine them separately.

II. Analysis of Charge.

In most cases the insoluble matter isolated as above consists mainly of inorganic substances. There may also be present lampblack, graphite, coal-tar dyes in the form of lakes, vegetable fibres, cork dust, starch, &c., not to mention residues of undissolved rubber. The charge is scraped out with a wooden spatula and closely inspected with the aid of a lens. Asbestos or cellulosic fibres, flake graphite, metallic powders, &c., will be recognized at once; lampblack also can often be recognized, and various clues as to the inorganic constituents may be obtained. The charge, unless it is to be analysed as a whole, must be ground and mixed thoroughly before being weighed out in portions, since the centrifugal process brings about a grading of the several powders in layers. Starch, which will now be present in the form of dextrin, is extracted by means of boiling water; it is a very unusual filler and occurs only in low-grade complex qualities. Tests for organic dyes, which occur more often in cold-cured than in heat-cured goods, are made by the usual methods; the dyes may, however, have escaped into the hot petroleum, or may have been extracted in the course of the earlier stages of analysis. The sys-

tematic examination of charge, in all ordinary cases, is conducted as follows :—

1. The material is treated with dilute hydrochloric acid, evolution of carbon dioxide or hydrogen sulphide being noted, and evaporated to dryness. The residue is again brought into solution by boiling with moderately strong (1 : 1) hydrochloric acid, then adding 200—300 c.c. of water, and boiling once more. In the case of red rubbers, a sufficiency of tartaric acid is added. If much lead be present, it may be desirable to decant and boil with fresh portions of water, without acid. The totally insoluble residue is filtered off, tested for absence of lead by a drop of ammonium sulphide, ignited in a platinum crucible, and weighed. In presence of carbon black, vegetable fibres, cork, ebonite, or residual rubber, the filter is previously tared (*e.g.* in the crucible itself) and is dried and weighed before ignition. To the ignited substance are added a sufficiency of pure hydrofluoric acid and a drop or two of sulphuric acid. After being evaporated down, the contents of the crucible are re-ignited and re-weighed.

In the first ignition, provided the residue be small or consist wholly of barium sulphate, the ignition loss will represent accurately enough the aggregate organic matter present. When there is silica in the residue, a certain amount of water, corresponding to the combined water of the siliceous matter, is included in the ignition loss and may be allowed for if the nature of the siliceous matter be known. Amorphous or graphitoidal carbon may thus be determined by ignition if uncontaminated with other organic matter ; but if such be present, carbon must be determined separately by the nitric acid method (see p. 155) either in the rubber or in the isolated charge.

Loss on evaporation with hydrofluoric acid indicates silica. Should it be small in amount, the loss may be set down to siliceous impurities or rubber-ash, and the residue (if white) regarded as pure barium sulphate. If, however, siliceous matter be present in any considerable quantity, the final residue in the platinum crucible should be fused with sodium carbonate or potassium bisulphate and assayed for barium and other bases in the usual way. The result, together with that of the hydrofluoric acid treatment ($= \text{SiO}_2$), provides the requisite quantitative data as to barytes and siliceous fillers.

Ferric oxide (rouge) and chromic oxide (green pigment) are in the main resistant to acid attack and behave in the same way as barium sulphate.

2. The filtrate from acid-insoluble matter is treated with hydrogen sulphide, when lead or antimony sulphide may come down. A precipitate of the former need be expected only in black or grey goods, of the latter only in red goods. Small quantities of lead are best determined gravimetrically: the precipitate together with the filter is moistened with concentrated nitric and sulphuric acids in a porcelain crucible, gently charred and burnt, ignited, and weighed as PbSO_4 . Larger amounts may be determined volumetrically by the following method¹:

The precipitate is decomposed with strong hydrochloric acid, diluted to 50 c.c., and treated with ammonia in very slight excess. Five c.c. of acetic acid are added, whereby the lead is again brought into solution. The liquid is heated to boiling and titrated with ammonium molybdate solution (8·6 gr. per litre), which is standardized against lead nitrate solution (16 gr. of $\text{Pb}(\text{NO}_3)_2$ per litre, 1 c.c. = 0·01 gr. of Pb). A dilute solution of tannin (5 gr. per litre),

¹ J. F. Sacher, *Chem.-Ztg.* 33 (1909), p. 1257.

sterilized with alcohol, serves as external indicator, giving a yellow coloration when the end-point is reached.

When the hydrogen sulphide precipitate consists of antimony sulphide, the metal is best determined gravimetrically as on p. 76. Lead and antimony are seldom, if ever, present together. In rubber compounded with black reclaims, however, a little antimony may occur side by side with lead and may be detected by extracting the mixed sulphides with sodium sulphide solution.

Vermilion is recognizable in rubber goods by its brilliant reds and pinks free from the slightest yellow or brown tone. In its presence, nitric acid must be added when the charge is decomposed by hydrochloric acid, otherwise it will not dissolve completely. All the mercury is then brought down by hydrogen sulphide. Mercury and antimony sometimes occur together, in which case the sulphides are separated by means of sodium sulphide.

3. The filtrate from the foregoing is boiled until free from hydrogen sulphide, filtered if necessary, and rendered alkaline with ammonia. An inconsiderable precipitate at this stage is usually due to mere impurities. A decided precipitate of alumina may represent a portion, extracted by acid, of the siliceous fillers present, and should be weighed as such. Iron is mostly a mere impurity, but in the case of goods pigmented with rouge or ochre is to be regarded as part of the pigment. Precipitates of calcium fluoride and phosphate are also possibilities; the former will have been introduced by barytes, the latter by bone-black.

4. In the filtrate, zinc is precipitated by boiling with an excess of ammonium sulphide. There are few pre-

cipitates so slow and difficult to filter as zinc sulphide, and therefore it saves time, at this stage, to halve the substance analysed, as follows :—

Precipitation having been effected, the whole liquid (of which the volume is presumed less than 500 c.c.) is immediately washed into a $\frac{1}{2}$ -litre measuring flask with hot water, made up to rather over the mark, and well shaken. The flask is left to itself until the precipitate has settled (1—2 hours) and is then further cooled with water, if necessary. Of the clear supernatant liquid 250 c.c. are siphoned off. Should the original volume of liquid fall short of 250 c.c., a $\frac{1}{4}$ -litre flask may be made use of in analogous fashion. In the clear half, calcium and magnesium, which are now the only metals left, are precipitated successively by means of ammonium oxalate and sodium phosphate; the results so obtained are multiplied by two. For greater accuracy, in measuring the hot liquid as above, a flask having 0·2 c.c. divisions on the stem may be used, the temperature of the liquid being noted; allowance ought also to be made for the volume of zinc sulphide, sp. gr. 3·3. For ordinary purposes, however, it suffices to fill up to an improvised mark corresponding to 15 c.c. in excess of the 500 c.c. bulk.

All the zinc is now left as sulphide at the bottom of the flask and may, if desired, be determined by the ordinary gravimetric methods. Filtration is best effected by means of a thick filter paper, or, still better, a nest of paper pulp. The sulphide may then be re-dissolved and the zinc re-precipitated as carbonate and weighed as oxide. A not much less accurate procedure consists in roasting the precipitated sulphide directly to oxide, after detaching the filter-paper as far as possible and burning it separately. Several hours' ignition in an open crucible, until the

smell of sulphur dioxide has passed away, will be required.

It is far more expeditious to determine the zinc volumetrically, for which the ferrocyanide method may be recommended. The whole remaining contents of the measuring flask are transferred to an ordinary flask, boiled up with a slight excess of hydrochloric acid to dissolve the sulphide, and titrated whilst hot with a solution of potassium ferrocyanide (35 gr. per litre, 1 c.c.=0·1 gr. ZnO approximately). The end-point is indicated by means of a 5 per cent. solution of uranyl nitrate, used as an external indicator: when all the zinc is precipitated, the red colour of uranyl ferrocyanide appears. The titrating solution is standardized against a solution of 10 gr. of pure zinc oxide in a litre of acidulated water; it keeps fairly well if preserved in the dark.

III. Special Determinations in the Charge.

When the charge has been submitted to the systematic analysis described in the foregoing section, the results will add up to less than full weight if the charge contains mineral matter other than barytes and simple oxides. Certain supplementary determinations may therefore have to be carried out, notably that of sulphide-sulphur and that of carbonic acid. Without a knowledge of these constituents it is often impossible to render a correct account of the qualitative nature of the compounding materials. Supplementary determinations postulate a good supply of isolated charge. When they are performed upon aliquot parts of a single lot of charge, it is most important that the charge be thoroughly ground and mixed before being broken into.

Combined Water (from silicates, calcium sulphate,

magnesium carbonate, etc.), can usually be estimated indirectly by calculation, and need be determined only in exceptional cases. The determination is carried out, preferably on not less than $\frac{1}{2}$ gr., by ignition in a current of dried air in a short tube-furnace (see p. 35), the water being caught in a calcium chloride tube. Organic matter in the charge will vitiate the results. In presence of volatile inorganic matter, e.g., antimony, a plug of asbestos should be placed in the cool fore-part of the ignition tube.

Total Sulphur is determined as on p. 131, and will then include the sulphur belonging to both sulphides and sulphates. To determine total sulphur other than that existing as BaSO_4 or PbSO_4 , 0·2—0·5 gr. of charge is assayed for acid-soluble total sulphur by the nitric acid method given for antimony pigment on p. 77. Acid-soluble sulphur minus sulphide-sulphur gives *soluble sulphate-sulphur*, which is usually present, if at all, as calcium sulphate.

Sulphide-Sulphur.—This may be present in large amount as zinc sulphide and in small amount as lead sulphide, either of which sulphides gives up practically the whole of its sulphur as hydrogen sulphide when decomposed by acid. In the case of antimony sulphide, the disengagement of hydrogen sulphide is not quite quantitative. To determine sulphide-sulphur, 0·2—0·5 gr. (or more, according to circumstances) of charge is weighed into an evolution apparatus fitted with a reflux condenser. The well-known Corleis flask (Fig. 20) does very well for this. Cheaper and equally serviceable is the apparatus shown in Fig. 21, which is made up from a dropping funnel, a ground-in wash-bottle, and a glass worm. The exit is connected with two successive absorption flasks,

each containing 50 c.c. of 10 per cent. zinc acetate solution. Air having first been expelled by a current of carbon dioxide, hydrochloric acid (1 : 1 for zinc sulphide, pure for lead sulphide) is introduced little by little and slowly brought to the boil. When all the hydrogen sulphide has been boiled off and driven over by means of

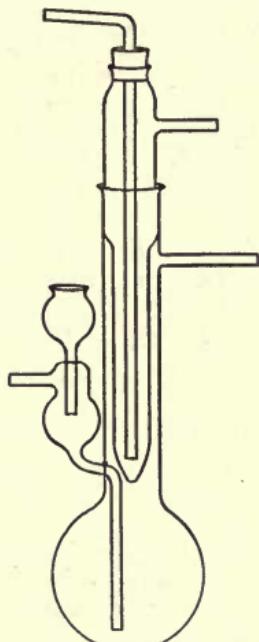


FIG. 20 (Scale 1 : 6).

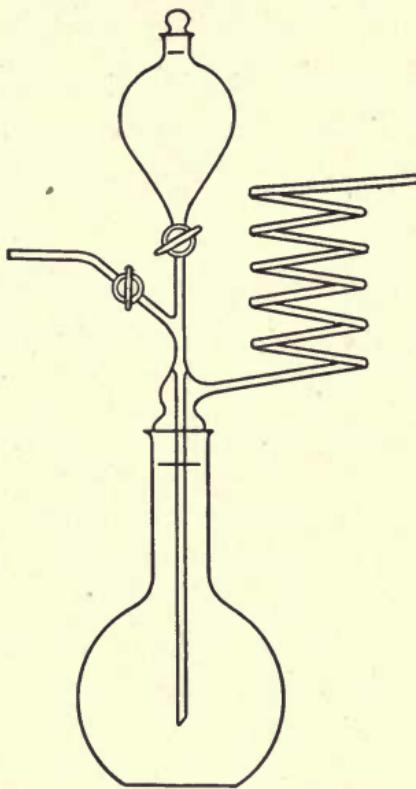


FIG. 21 (Scale 1 : 5).

carbon dioxide, the united contents of the absorption-flasks are thoroughly shaken with 50 c.c. of $N/10$ iodine solution, the excess of which is titrated back with thiosulphate. One gr. of iodine = 0.1263 gr. of sulphur.

Carbonic Acid may be present as calcium or magnesium carbonate, exceptionally as lead carbonate ; its determination is at least as important as that of sulphide-sulphur

and is carried out by means of the same apparatus. The substance is first covered with cupric sulphate solution—to retain hydrogen sulphide—and then decomposed with dilute (1 : 10) hydrochloric acid, very slowly added. The liquid is eventually boiled and the carbon dioxide swept over by means of purified air. Absorption is effected in Geissler bulbs or soda-lime tubes, which must be preceded by at least one calcium chloride tube to retain moisture.

Phosphoric Acid, which is but rarely present, may be determined in the usual way by precipitating a nitric acid extract of the charge with ammonium molybdate reagent.

IV. Notes on the Interpretation of Charge-Analyses.

Of the various organic substances which may be embraced in the ignition loss of the acid-insoluble portion, finely-divided *undissolved rubber* points to the presence of reclaim or ground waste, unless the sample as a whole is obviously over-cured. Its amount, when ascertained, should be deducted from charge proper. *Carbon* may be separated from rubber, and other organic matter, by the nitric acid method (p. 155), and should be determined separately whenever it does not happen to be the sole combustible constituent. Carbon may have been imported by coal-tar pitch (see p. 56) or black hypo (see p. 82). Amorphous carbon may be distinguished from graphite by the relatively difficult combustibility of the latter. Among less common organic substances may be mentioned *saw-dust*, *cork dust*, *ebonite dust*, *cellulosic fibres*, etc., which sometimes occur in brake-blocks and the like. These remain with the charge when the rubber is broken down by means of petroleum and can then be approximately determined by ignition loss. The original mineral con-

stituents of ebonite dust, like those of reclaim or ground waste, will in most cases, however, prove inextricable from the mineral charge proper.

In the acid-insoluble portion of the charge we have all the barium (which hardly ever occurs in rubber goods except as sulphate), all the silica, and most of the bases combined with silica as silicates. If silica be present uncombined, *atmoid* or *talite* is indicated. When alumina is the principal silicate-base in a white residue, *kaolin* is indicated; in coloured residues, *ochre* or *slate-powder*. Magnesia as a base points to *talc*; *asbestos*, which can usually be recognised as such, sends most of its magnesia into acid solution. Fancy silicates such as *pumice*, *mica*, *glass*, etc., are peculiar to special classes of goods and can often, moreover, be detected by inspection under the lens.

The form in which lead occurs in a rubber article is in nine cases out of ten *litharge*. This may be detected as a heavy yellow powder, and thus distinguished from white lead, when the isolated charge is shaken up with a liquid, as in the course of the isolation process itself. *White lead* is less easy to make sure of; but in many cases the carbonic acid and sulphate-sulphur afford a clue. All heat-cured goods made up with lead compounds contain a small quantity of *lead sulphide*. Antimony and mercury are never present except as sulphides; the former will frequently be found to be accompanied by calcium sulphate.

Zinc may be present in the form of oxide or sulphide (as such or in lithopone) or both. When there is little or no sulphide-sulphur in the charge, *zinc white* may be confidently diagnosed. So much sulphide-sulphur (apart from lead sulphide, which is mostly negligible) as is not

accounted for by antimony or mercury may be presumed to be in combination with zinc. If, then, this sulphur and the zinc present are in approximately equimolecular proportion, *zinc sulphide* alone is indicated; if there is a deficiency of sulphur, zinc oxide and sulphide side by side. Barium sulphate and zinc sulphide in equimolecular proportion point, almost certainly, to *lithopone*.

The variety of forms in which calcium may occur is apt to give trouble in interpretation. Sulphate-sulphur soluble in acid may be assumed to be combined with lime; *calcium sulphate* very commonly occurs in red rubbers, but seldom elsewhere. Calcium in large amount points to *whiting*, and this can be checked (in absence of magnesium) by the carbonic acid present. Small amounts (2—5 per cent.) are probably present as *caustic lime*, so far as they are not of the nature of impurities. It is not easy to make sure of this body in company with carbonates; useful qualitative indications can often be obtained by testing an aqueous extract of the charge for alkalinity.

Of magnesia it may similarly be said, in general, that considerable quantities indicate *magnesium carbonate*, small quantities *calcined magnesia*. Some control can be effected by careful determination of the carbonic acid, it being remembered that commercial light magnesium carbonate contains only about 40 per cent. of CO_2 . When *asbestos* is present as a filler, magnesia derived therefrom (up to about 30 per cent. of MgO upon the silicate) may be encountered in the final stage of mineral analysis.

V. Special Determinations in Original Material.

1. *Sulphur*.—The total sulphur in a manufactured rubber article is determined by treating the comminuted,

but otherwise untouched, material by the nitrate or peroxide method, as described on pp. 128—131.

The necessity for determining total sulphur, however, seldom arises. On no account should sulphur present in a given form (*e.g.* sulphur of vulcanization) be estimated by the difference between total sulphur and sulphur in other forms: the chances of large error greatly outweigh those of accurate determination. It may here be useful to recapitulate the various forms in which sulphur may occur in rubber goods:—

1. Free (pp. 115—117).
2. Combined with factice (p. 125).
3. Combined with rubber and bitumen (pp. 128—131).
4. In mineral combination (p. 131):—
 - a. Barium sulphate (p. 150).
 - b. Sulphides (p. 150).
 - c. Soluble sulphates (pp. 150—151).

The sum of Nos. 1 and 3 constitutes sulphur incorporated as such in the original mixing.

2. *Carbon*.—When quantitative data as to the amorphous carbon or graphite in a rubber are required, it is often advisable to make a special determination starting from original material. To this end, advantage may be taken of the fact that the organic portion, and much of the mineral matter, is converted into soluble bodies by the action of nitric acid, whilst carbon is not attacked to any serious extent. The comminuted rubber (1—2 gr.) is evaporated with 20 c.c. of nitric acid in a small porcelain basin on a water-bath. Evaporation is repeated, if necessary, with fresh acid until no more lumps of undecomposed rubber can be detected. The contents of the dish are rinsed into a beaker and boiled with 400 c.c.

of water, when rubber-nitration products and more or less inorganic matter go into solution. The settled liquid is sent through a tared filter; the residue is twice washed by decantation with hot water, brought on to the filter, and thoroughly washed out with hot water. The contents of the filter are now rinsed back into a small beaker and warmed with 50 c.c. of dilute ammonia, which dissolves the remaining nitro-compounds. A pinch of ammonium chloride should be added to precipitate colloidal carbon. Any floating grease (derived from bitumen or paraffin) still present is removed by extraction with ether. After settling, the clear liquid is poured through the original filter, and the process of boiling up the residue with ammonia and ammonium chloride, settling, and decanting, is repeated so long as yellow solutions are formed. Finally the residue is boiled up with 100 c.c. of dilute hydrochloric acid, returned to the original filter, well washed, dried at 110°, and weighed. We now have carbon plus mineral matter, the latter consisting essentially of barium sulphate and silicates. The weighed filter is therefore incinerated and the weight of mineral matter duly subtracted.

Sufficiently accurate results can thus be obtained by weighing the actual carbon in all cases when there is a reasonably large amount of it, and the residual minerals consist mainly of barium sulphate. Siliceous matter introduces an error owing to its water of hydration. When there are several centigrammes of siliceous matter, and in general when the minerals are much in excess of the carbon, the latter should be determined by combustion. For this purpose the insoluble residue is collected, not on a paper filter, but on ignited asbestos in an untared Gooch crucible or similar contrivance. Asbestos and substance are then dried, transferred unweighed to a

boat, and burnt in a small tube-furnace, the carbon being weighed as CO_2 .

3. *Antimony and Mercury.*—The necessity frequently occurs of determining these metals by a separate assay, especially in ebonites and in other materials where the bulk of the mineral charge is dealt with by ash-analysis. The first thing to do, in such cases, is to destroy the rubber and other organic matter in the wet way. Several methods, each of which has its devotees, have been proposed, *e.g.* by J. Roth¹ (sulphuric and nitric acids), F. Frank and C. Birkner² (ammonium persulphate and nitric acid), and W. Schmitz³ (sulphuric acid and mercury). Sulphuric acid acts satisfactorily enough, and the addition of mercury may well be dispensed with. The following procedure may be recommended :—

Two gr. of rubber are heated with 25 c.c. of concentrated sulphuric acid in a long-necked Kjeldahl flask, loosely stoppered with a small funnel. After the first effervescence has subsided, the liquid is left to boil briskly, over the free flame, for two or three hours. It is then cooled, and 1 gr., or more if necessary, of potassium permanganate crystals is cautiously added. On boiling again for a short time, the liquid assumes a light reddish-yellow tint, and there is now no need to continue the destructive process. The cooled magma is taken up with 300 c.c. of water, boiled up, and filtered. In the clear filtrate, antimony or mercury is precipitated by means of hydrogen sulphide. If antimony alone be present, it is determined in the usual way. In presence of both metals, the sulphide precipitate is collected on a tared

¹ *Chem.-Ztg.* **33** (1909), p. 679.

² *Chem.-Ztg.* **34** (1910), pp. 34, 49.

³ *Gummi-Ztg.* **25** (1911), p. 1928.

filter, washed, rinsed into a small beaker, and warmed with sodium sulphide solution. The undissolved mercury sulphide is returned to the filter and washed, and in the filtrate antimony is reprecipitated by acidification. Meanwhile the bulk of the mercury will have remained, together with other fillers, in the undissolved sulphate residue; this is now therefore gently boiled for some time with moderately strong hydrochloric acid. After filtering, and testing the residue with ammonium sulphide, the clear solution is treated with hydrogen sulphide; the precipitate of mercuric sulphide is added to that which is already on the tared filter, washed with water slightly acidified with hydrochloric acid, then with alcohol, then with carbon disulphide, dried, and weighed.

VI. Ash-Analysis.

Any unimpeachably correct method for ascertaining the amount and composition of the charge in a vulcanized rubber would have to be based on the destructive dissolution of the rubber-substance. But such a process as that described on pp. 141—143 is comparatively troublesome and necessitates the use of costly apparatus. On the other hand, incineration is a rapid, easy, and, within its limits, exact operation, but it has the defect of obscuring the true nature of the charge to some extent. The effect of incineration on the more usual filling materials may be expressed by the following classification:—

No change in the main :—Barytes, Zinc White, Iron Oxide, Calcium Carbonate, Magnesia.

Loss of combined water :—Calcium Sulphate, Lime, Infusorial Earth, Kaolin, Asbestos, Talc.

Loss of carbonic acid and water :—Magnesium Carbonate, White Lead.

Volatilization :— Sulphur, Vermilion, Lampblack, Graphite, Organic Fibres and Powders.

Partial Reactions :— Litharge combines with sulphur and oxygen to form lead sulphate; so much as is present in excess of the available sulphur remains unchanged, being sometimes partially converted into minium. Zinc Sulphide is more or less roasted to oxide, according to the duration and intensity of ignition; a little sulphate may also be formed. Antimony Sulphide is converted into tetroxide; occasionally the metal is recovered quantitatively from the ash, more usually it undergoes partial volatilization. Whenever accurate information as to its amount is desired, antimony, like mercury, should be determined separately in the rubber itself. Caustic Lime and Magnesia combine with as much sulphur as they can seize and yield sulphates to a corresponding extent; the same tendency, in a comparatively modest degree, is observed with Zinc White and Magnesium Carbonate. A certain amount of reaction in this sense, negligible for ordinary purposes, will have already taken place during vulcanization (*cf.* p. 111). Lime, so far as it is not sulphated, is converted into carbonate.

It will be gathered from the above that the percentage ash of a compounded rubber will generally come out slightly lower, less usually slightly higher, than the true total charge. Unless, however, there be much magnesium carbonate, carbonaceous matter, or vermillion present, or, on the other hand, much sulphur in conjunction with basic materials, the difference will not be intolerably great, as rubber standards go. This discrepancy affects the determination not only of charge but also of rubber; but it can to a large extent be neutralized by a knowledge of the nature of rubber goods generally and by certain

supplementary analytical operations. In commercial specifications it is still customary to impose limits on the percentage, not of true charge, but of ash; which, in view of the ease and cheapness of ash-determinations, seems quite proper. As regards the detailed composition of the original charge, the direct results of ash-analysis undoubtedly yield but a distorted image. The same, however, applies to some extent to analysis of the charge isolated as such. An analyst who is capable of interpreting the one will probably be equal to the other, so far as exact interpretation is possible at all. On the whole, then, the cases in which ash-analysis, plus supplementary determinations, fails to yield all such information as is obtainable are less common than might be supposed. Even such lacunæ as sulphide-sulphur and carbonic acid can generally be filled up deductively. Almost the only determination for which isolation of the charge is absolutely indispensable is that of sulphur of vulcanization in goods containing inorganically combined sulphur.

In the incineration of vulcanized rubber it is desirable to avoid high temperatures and lengthy ignition as far as possible, so as to reduce decomposition of calcium carbonate and partial volatilization of metals to a minimum. The dissipation of volatile organic matter should be carried out slowly and without allowing the vapours to burst into flame, since excessive local temperatures might then be produced at the surface. Of heavy rubber 1 gr., of medium 2 gr., and of floating 5 gr., cut into smallish pieces or crumbed, are weighed into a tared porcelain dish of about 8 cm. diameter. The best form of dish is neither flat nor hemispherical, but the intermediate shape. As the dish is cautiously heated over a Bunsen flame, the rubber, unless very highly charged,

melts and presently fumes off with ebullition. There need be little or no charring, since rubber, resins, waxes, and bitumens are volatile with very little organic residue. When no more fumes are disengaged, the dish is transferred to a muffle and ignited at a low red heat until the ash is free from carbonaceous matter. As a rule, neither the first nor the second operation need last more than ten minutes. The clearing of the ash by ignition proceeds rapidly, owing to the porosity of the mineral matter and its catalytic effect on combustion. Litharge should not be allowed to fuse nor calcium carbonate to dissociate; that is, the temperature should not rise much above 700°. Magnesium carbonate is wholly reduced to oxide. Lamp-black burns off very readily, but in presence of graphite, which is less easily combustible, there is nothing for it but to take the risks attendant on prolonged ignition. Zinc reveals itself by a brilliant yellow coloration of the hot ash, which disappears on cooling. In a busy laboratory it is well to number the dishes,—best with an argentiferous marking ink,—and keep a list of their approximate tares near the balance.

The contents of the dish are treated with cold *dilute* hydrochloric acid. Effervescence of carbon dioxide indicates calcium carbonate. If the ash goes completely into solution, lead, antimony, and silicates are absent; if there is a residue, *strong* hydrochloric acid is added. Evolution of hydrogen sulphide at this stage generally indicates zinc sulphide; but the presence of this body in the original rubber is to be inferred only if the disengagement of hydrogen sulphide is somewhat considerable, since sulphides in small amount may be produced during incineration. Evolution of chlorine points to minium, probably of secondary formation. The contents of the

dish are transferred to a beaker, diluted, and boiled for some time to bring lead and antimony into solution.

A trouble often experienced at this stage is caused by the difficult solubility of antimony tetroxide. When there is a large ballast of other inorganic matter, the antimony is usually so finely divided that it can be dissolved by prolonged boiling with hydrochloric and a little tartaric acid. But with goods containing little else than antimony-red as charge (*e.g.* red inner tubes, high-class sheet, &c.), the ash is apt to sinter into a hard enamel which is practically insoluble, though relief may sometimes be obtained by fusion with potassium bisulphate. The best plan in such cases is to cover the ash with powdered ammonium chloride and re-ignite; most of the antimony is thereby volatilized, whilst the little that remains no longer offers an obstacle to the determination of non-antimonial matter.

The insoluble residue, consisting of barium sulphate and silicates, is filtered off, washed, and tested for lead by means of ammonium sulphide. As a rule, the appearance of the residue will afford a clue as to whether much siliceous matter is present. Should this not seem to be the case, the residue is ignited and weighed in a platinum crucible, then evaporated with hydrofluoric and sulphuric acids, re-ignited, and re-weighed. The difference in weight, if considerable (*e.g.* more than a centigram), will represent something more than ordinary siliceous impurities, and in this case it is safer, in order to determine barium sulphate accurately, to fuse the residue in the crucible and determine barium in the lixiviated melt. Total acid-insoluble matter other than barium sulphate and coloured sesquioxides may be set down to silicates; but it is to be noted that additional instalments of the silicates originally present are almost sure to be

encountered in the subsequent group-separation, hydrous silicates being much more susceptible to acid attack after ignition than before. The nature of the silicates may be gathered from their qualitative composition, as ultimately ascertained.

Should the acid-insoluble portion of the ash be suspected from the beginning of being largely siliceous, it is advisable, instead of treating with hydrofluoric acid, to fuse with sodium carbonate directly after igniting and weighing, and to analyse as usual.

The acid-soluble portion of the ash is dealt with by the ordinary group-separation methods sketched out on pp. 145—149.

We now have to consider the relations existing between the results of ash-analysis and the original mineral components of the rubber. The task is a double one. In the first place, corrections have to be applied to each analytical item so as to translate ignited into terms of original charge. In the second place, the amount and nature of the several compounding materials have to be deduced from the immediate analytical data. As aids to recalculation, the following points may be noted:—

Barium sulphate may be set down to *barytes* or *lithopone*.

Siliceous matter covers the ash of raw rubber, impurities generally, and the usual siliceous fillers. Most silicates lose some combined water (4—12 per cent.) on ignition; when, therefore, the identity of the silicate has been decided upon, the proper plus correction should be made.

Lead, in the great majority of cases, exists in the ash as sulphate but was originally present as *litharge*; a corresponding minus correction is therefore to be made. If

the ash visibly contains much litharge as such, the best course, on the whole, is to make no correction for sulphatization; in case there is no other sulphate or sulphide present beside barium sulphate, the actual amount of sulphated lead can, however, be ascertained by a determination of total sulphur in the ash. *Red lead*, *white lead*, *black hypo*, and *lead sulphide* are comparatively uncommon fillers. When they do occur they cannot well be traced in the ash, but indications may often be obtained by testing the shredded rubber with concentrated hydrochloric acid.

Antimony generally comes out too low in the ash, and should be separately determined. It may be calculated to Sb_2S_3 or Sb_2S_4 . Whenever antimony occurs, it is well to look out for calcium sulphate.

The Group III (ammonia) precipitate yielded by a white ash is in most cases insignificant and due mainly to impurities. A respectable precipitate of alumina, carrying with it some silica, points to silicates; *kaolin*, for instance, sends almost the whole of its alumina into acid solution after ignition. Phosphate and fluoride precipitates (from *bone-black* and *fluorspar* respectively) are easily recognized and may be dealt with by the usual methods. *Rouge* and *ochre*, which give rise to precipitates in this group, will already have revealed themselves in the ash if not in the rubber itself.

With zinc it is sometimes difficult to decide whether the oxide or the sulphide was originally present, more especially when the quantity is small. The complete conversion of sulphide into oxide requires very prolonged ignition; hence, given a reasonable quantity of zinc, a decided evolution of hydrogen sulphide with acid indicates *zinc sulphide*, whilst little or no evolution indicates *zinc*

white. Barium and zinc in approximately equimolecular proportions point to *lithopone*. This latter pigment often occurs together with zinc white, fairly often with barytes, but hardly ever with added zinc sulphide.

Calcium may have been present originally as carbonate, hydroxide, or sulphate. The sulphate is very rarely met with except as a constituent of *antimony red*. The ash of red rubbers will therefore frequently contain calcium. When Ca is found in any amount up to one-half of the Sb, it may fairly safely be regarded as belonging to the pigment, and may be calculated as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Calcium in excess of this limit will probably be due to whiting. In rubber-ash generally, soluble sulphates, so far as they cannot be accounted for as reaction-products of litharge, lime, and magnesia, may be ascribed to calcium sulphate. Carbonic acid determined in the ash may be taken to represent *whiting*, with the proviso that any hydroxide originally present will in most cases emerge from the incineration process in the form of carbonate. Hence, if caustic lime and whiting occur together, they cannot be disentangled in the ash. Small quantities of calcium, say up to 5 per cent. of CaO on the rubber, indicate *caustic lime*, and may be calculated to $\text{Ca}(\text{OH})_2$. Larger quantities are best calculated to CaCO_3 , and assumed to be due to whiting alone. Special quick-curing rubbers, however, may contain rather considerable percentages of caustic lime.

With magnesium, again, there is often a doubt as to whether oxide or carbonate was originally present, since both are found as oxide in the ash. Here, as in the case of calcium, one must be guided by the fact that the oxide is essentially an accelerator of vulcanization and the carbonate a filler. *Calcined magnesia* is seldom put into

a mixing other than that of the quick-curing type to more than 10 per cent., whilst carbonate may occur in any quantity. Much *magnesium carbonate* (30 per cent. or over), unlike whiting, makes a very stiff rubber, and may therefore be suspected from the beginning. On the other hand, it is unsafe to assume that small quantities of magnesium necessarily indicate oxide rather than carbonate. In the absence of calcium, magnesium carbonate may be detected in the finely-divided original rubber by means of dilute hydrochloric acid.

Both calcium (in very small amount) and magnesium originating from silicates may find their way into the acid extract of an ash. Similarly, a portion of the calcium of bone-black may persist into the oxalate precipitate.

CHAPTER IX

GUTTA-PERCHA AND BALATA

THE industries of which these gums are the raw material are commonly carried on side by side with the manufacture of rubber goods, though the technique is in almost all respects quite different. Gutta-percha and balata are obtained from the latex of trees which are botanically unrelated to the rubber-bearing species, and by a distinct method of collection. The former gum is also to some extent extracted, by mechanical means and by the aid of solvents, from leaves and other parts of the tree. Gutta-percha comes from the Malay Peninsula, Sumatra, Borneo, and neighbouring countries, whilst balata has its place of origin in Venezuela and the Guianas. Gums passing under the name of balata, but differing somewhat from Venezuela balata, especially in the associated resins, are moreover imported from the Amazon Valley, West Africa, and elsewhere. Gutta-percha and balata consist essentially of an amorphous colloidal hydrocarbon chemically indistinguishable from that of india-rubber, together with a large proportion of resin. The specific gravity of the isolated hydrocarbon is 0·96, that of the resinous gum

being usually just short of unity. In spite of the chemical similarity, these hydrocarbons differ widely from rubber hydrocarbon in physical respects. When cold, they are of a firm tough consistency suggestive of the denser sorts of leather; under shearing stress they are eminently pliable, and recover from deformation incompletely and somewhat sluggishly; tensile and compressile elasticity are all but absent. This peculiar mechanical "deadness" is much enhanced by the presence of resin. At temperatures well below 100°, gutta-percha and balata soften without developing the marked tackiness of uncured rubber, and in that condition they are highly plastic and ductile and lend themselves admirably to all kinds of moulding operations. This property, together with their toughness and high electrical insulation when cold, constitutes their chief claim to utilization in the arts. Balata hydrocarbon shows considerably more springiness under shearing stress than gutta; but for many practical purposes no very sharp distinction is made between the two gums. By far the greater part of the gutta-percha imported into Europe goes into cable-coverings, especially for submarine work; the remainder is made into various small articles of surgical, chemical, and mechanical utility. Balata, as such, is notably applied to the manufacture of lined canvas belting. The technology of gutta-percha and balata resolves itself into processes of washing and drying, softening by heat, shaping, and cooling. Vulcanization is not practised. Compounding materials are only exceptionally added, and usually in small proportion. On a moderate scale the de-resinification or "hardening" of gutta-percha and balata by extraction with solvents is carried out industrially, raw gutta-percha of low resin-content being much scarcer now than formerly.

Crude gutta-percha is composed of twists, sausage-shaped rolls, and large lumps of rounded or rectangular contour, always containing moisture and a good deal of bark and other dirt. It is even more inhomogeneous than crude rubber, because the separate pieces in a package commonly differ not only in washing loss but also in quality and resin-content. Attempts at sampling crude gutta-percha are therefore apt to be illusory, and it is advisable to postpone analysis until the whole package has been washed and sheeted. Washing losses usually run from 20 to 50 per cent. In dealing with a hand-sample, a proportional fragment may be cut from each piece, so as to make up a sample for analysis; but even in this case it is sounder practice to determine moisture on the whole lot, then mix on the rollers, and then continue the analysis. *Extracted gutta-percha* usually takes the form of neat blocks homogeneous in composition and nearly free from moisture and dirt. *Crude Balata* of the Venezuelan type comes over in large thick slabs and blocks, which are as a rule much cleaner and more homogeneous than crude gutta-percha. A considerable quantity of *recovered gutta-percha*, mainly cable-strippings, comes into the market and is used up again without any special treatment save removal of mechanical impurities. Old gutta-percha which has served on land will generally have become partially resinified, whilst with submarine goods this effect is only slight; but in either case the gutta hydro-carbon will have deteriorated by partial loss of plasticity and cohesion.

The commercial value of gutta-perchas and balatas obviously depends in a high degree on washing loss and resin-content; but apart from this there are notable variations in the mechanical quality of the gutta hydro-

carbon, as also in the insulation-resistance of the washed and dried gums.

Analysis of Gutta-Percha and Balata.

The analytical procedure is the same for raw and manufactured material, and consists in the determination of moisture, resin, dirt, and hydrocarbon (termed "gutta" for short). No analytical distinction is made between the hydrocarbons of gutta-percha and balata, but there are various indications on which an identification can often be successfully based, provided that the one or the other be present alone or in decided predominance.

Moisture.—One to five gr. (or more in the case of crude gum), cut into snippets, are spread on a flat dish and dried to constant weight in the vacuum-oven at 95°. Three hours should be given as a minimum, but with comparatively moist samples a much longer period may be requisite. An alternative method consists in heating for three hours and upwards at 110° in an atmosphere destitute of oxygen, the apparatus being of the type referred to on p. 24. Dried carbon dioxide is the indifferent gas ordinarily used, but dried coal gas serves practically as well, since gutta-percha is much less apt to absorb matter from it than india-rubber.

Resin.—The ratio of gutta to resin in crude gutta-percha varies between wide limits, from about 3:1 in the finest reds to about 1:3 in low whites. In balata the ratio is about 1:1. Manufactured gutta-percha of ordinary quality may be expected to show ratios ranging between two of gutta to one of resin and equal parts. The determination of resin is carried out by either of the two methods described below. Original material may be taken for assay if the moisture-content amounts to only

a few per cent., as is the case with the majority of manufactured goods; otherwise the material should first be dried.

1. *Extraction Method.*—The material is cut with the aid of a knife and scissors into the finest possible snippets. Of these, one or two gr. are extracted with acetone exactly as in the case of rubber, except that a Soxhlet extractor is employed. At the comparatively low temperature of the Soxhlet, gutta-perchas do not, unless abnormally soft, cake by partial fusion. Ten hours suffice for complete extraction, whereupon the extract is evaporated and dried for three hours at 110°. This method of resin-assay is not only the least laborious but also the most accurate; its only drawback is that a good deal of time elapses between start and finish.

2. *Precipitation Method.*—One gr. of material, which need not be finely comminuted, is placed in a 100 c.c. Erlenmeyer flask with 20 c.c. of redistilled toluene or solvent naphtha, heated to 100° on a water-bath, and vigorously shaken until solution is complete. The liquid is poured, with agitation, into 50 c.c. of ordinary alcohol in a rather larger Erlenmeyer, whereby gutta is precipitated; the contents of the first flask are also shaken up with alcohol and added to bulk. The last traces of gutta come out of solution somewhat reluctantly; it may therefore be necessary to warm and shake very thoroughly until the solution is clarified. The clear liquid is poured off and set aside, and the residual clot of gutta is washed by kneading with alcohol, redissolved, and again precipitated. With highly resinous gutta-perchas the process should be repeated once more. The united clear alcohol-toluene liquors are distilled from a capacious tared Soxhlet flask, and the residual resin is dried to constancy.

and weighed. The precipitated gutta, which carries with it all the dirt originally present, may be dealt with quantitatively as described below.

The resin obtained from ordinary gutta-perchas is of a pale amber colour and semi-hard consistency; that from inferior white sorts is sometimes completely hard and brittle. Gutta-perchas extracted from leaves and twigs

yield soft resins of a characteristic green colour. Balata resin, when fresh, is a thick treacly fluid. Resins extracted from manufactured goods may be affected as to colour and smell by the presence of a little tarry or bituminous matter.

Dirt and Fillers.—Gutta-percha owes its brown colour to the invariable presence of a few per cent. of finely-divided humus, which cannot be completely removed by washing. Balata contains less of this impurity, or none at all. The presence of pulverulent compounding materials can generally be recognized at first sight; the most usual ones are the pigments zinc white, lithopone, antimony red, and carbon black, also

talc, kaolin, and other silicates acting merely as fillers. With the exception of the three pigments last-named, mineral admixtures are most conveniently determined by incineration. By far the greater number of manufactured goods contain no intentionally added solid matter. Dirt in gutta-percha may be determined as follows:—

1. *Pontio's Method.*—This is based on the fact that

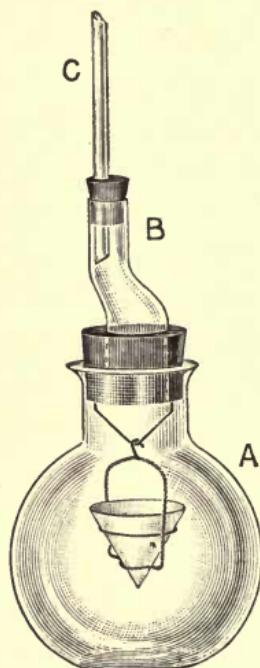


FIG. 22a.

gutta-percha is readily liquefied by toluene in the form of vapour, and is a remarkably convenient and accurate, though somewhat slow, method. The material, which must contain only a few per cent. of moisture, is roughly cut up, and 1 gr. is weighed into a tared 7 cm. ashless filter of medium density (*e.g.* Schleicher and Schüll's "White Band") folded into the usual conical form. The filter is fitted into a cage of copper or nickel wire, which is suspended in the vapour of toluene boiling under reflux condensation. For one filter only, the simple outfit shown in fig. 22a serves very well. *A* is a 250 c.c. Soxhlet flask, aperture about 4 cm., in which 50 c.c. of toluene are kept boiling on a sand-bath; *B* is a bayonet-shaped adapter, the sole aim of which is to prevent condensed drops from falling into the filter; *C* is an air-cooled condenser which may consist of a simple upright tube or a spiral worm. Embedded in the lower cork is a wire stirrup which carries the cage. If the bottom of the adapter be kept flush with this cork, or slightly higher, the condensed toluene will return down the sides of the apparatus and there will be no danger of splashing. Fig. 22b shows a ground-in modification of the same apparatus, with which the inevitable slow loss of solvent attendant upon the use of cork is avoided; this apparatus also does very well for alcoholic potash extractions (*cf.* p. 35). For conducting three, four, or six dirt-

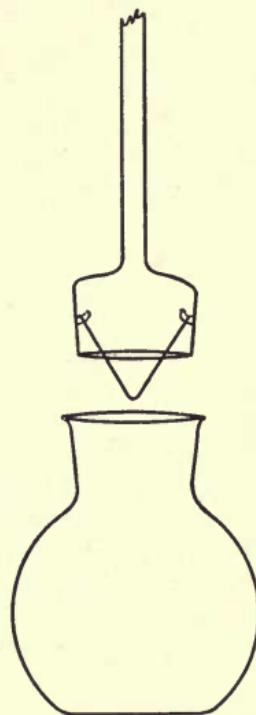
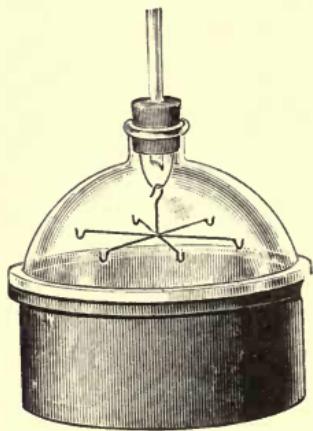
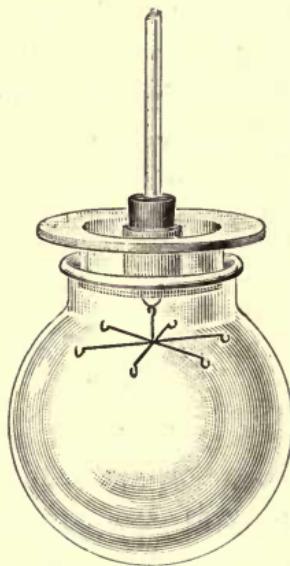


FIG. 22b.

determinations at once, large boiling-vessels of the type of Fig. 23*a* or Fig. 23*b* are used, the filter-cages being suspended from six-rayed stars of stout wire. Apparatus *a* is really a laboratory vacuum-still; the flange of the glass upper half is clamped to that of the metal or porcelain lower half by means of three small wooden vices; a leather washer is interposed, or, if the flange-surfaces be very true, the connexion can be rendered tight with a mixture of glucose syrup and glycerine. In apparatus *b*

FIG. 23*a* (Scale 1:6).FIG. 23*b* (Scale 1:7).

the thick glass globe, aperture about 11 cm., is fitted with a flat glass ground-in stopper having a central tubulure. The six-filter apparatus devised by M. Pontio, which is intended for other determinations beside that of dirt, consists of apparatus *b* with an extensive superstructure. Mercury lutes are undesirable in vapour-extraction apparatus, since drops of volatilized and condensed metal are apt to find their way into the filters.

Under the action of toluene vapour, the gutta-percha

is liquefied and gradually passes through the filter, leaving solid impurities behind. The time required is rarely less than ten hours and sometimes considerably longer. It may happen that the solids are so fine as to choke the filter and prevent the solution from traversing it in reasonable time; in this case relief may often be obtained by substituting xylene or solvent naphtha for toluene, so that the filter is exposed to higher temperatures. Again, some materials form solutions too viscous to be filtrable; this is especially likely to occur with balatas and "hardened" gums. Dirt will then have to be determined by the alternative method given below. These exceptions apart, the method works smoothly and is widely applicable.

2. *Sedimentation Method.* One or two grammes of material are dissolved in 100 c.c. of hot benzene or similar solvent and rinsed into a wide test-tube or Nessler glass, which is then corked and left to itself on a water-bath. The dirt sinks to the bottom within two or three hours. As much as possible of the transparent solution is siphoned off without disturbing the sediment, which latter is brought on to a tared filter or Gooch crucible and thoroughly washed with solvent, or—still better—exposed for half an hour to toluene vapour. The filter is dried at 110° and weighed. This method, though comparatively laborious, yields results within a few hours, and may be yet further expedited by the use of a centrifuge, in which case the volume of solvent should be cut down to 50 c.c.

Whilst washed balata is remarkably poor in dirt, washed gutta-percha always contains from 2 to 6 per cent. of impalpable humus. These natural impurities usually contain about 20 per cent. of mineral matter. The ash of a gutta-percha incinerated as such generally comes

out a little higher than that of the isolated dirt, because traces of metallic humates and resinates are dissolved out by toluene. Gutta-percha solutions are always slightly coloured, whereas balata solutions are almost water-white. In any case, the total ash of washed gutta-percha should not exceed 1·5 per cent.

Pulverulent fillers may be determined together with the dirt, but it is to be noted that the more fine-grained sorts of pigment are apt to pass through the filter in colloidal suspension. Accurate determinations are best effected by the aid of the centrifuge (*cf.* p. 142).

Factice is determined after acetone extraction exactly as in the case of rubber (see p. 123). A few tenths per cent. of saponifiable matter are almost always extracted by alcoholic potash from factice-free material. As an admixture, factice is rather uncommon, and is never present in any considerable proportion.

Bitumen and Pitch, unless present in mere traces, are detected by the brown colour which they impart to solutions of the material. Pitch, moreover, is indicated by its fluorescence in solution and by the presence of finely-divided carbon. Approximate quantitative determinations are effected by the method described under "Chatterton's Compound," due regard being had to the fact that more than one-half goes into the acetone extract.

Gutta. In most cases it suffices to estimate gutta by difference. When it is desired to determine gutta directly, the method to be adopted consists in precipitating the hydrocarbon from benzene or toluene solution by means of alcohol. Solid matter other than mere dirt should first be eliminated. This is best done by rinsing the solution into a measuring cylinder or flask, making up to

the mark, and allowing the insoluble to settle out; an aliquot part of clear liquid is pipetted off, and in this the gutta is precipitated. Precipitation is effected as on p. 171, and should be repeated at least once. Ultimately the clot of gutta is boiled out with clean alcohol, transferred to a flat tared dish, dried *in vacuo* or in indifferent gas, and weighed. The gutta will contain all the solid impurities which were present when it was precipitated, so that these may have to be determined in the weighed gutta and duly taken into account. The guttas isolated respectively from gutta-percha and balata may be distinguished, apart from the peculiarities of colour mentioned above, by the fact that in equivalent solutions balata hydrocarbon is about twice as viscous as gutta.

Chatterton's Compound.—This is a watertight cement prepared by boiling gutta-percha with Stockholm tar, often with the addition of rosin or bituminous substances. Its value depends mainly on the amount of gutta present. Volatile matter, which will include moisture, is determined by the method described under "Moisture." By acetone extraction gutta-percha resin and added rosin are isolated, together with so much of the tar as does not consist of volatile matter or carbon. The extracted residue is dissolved in ten parts of benzene; if the settled solution is light in colour, it will contain nothing but gutta, apart from the sediment. If the colour is brown, the presence of bitumen is indicated. In that case the solution is reprecipitated three times with just twice its volume of alcohol; the clear united benzene-alcohol solutions will then contain bitumen insoluble in acetone, whilst gutta and dirt compose the residue. Dirt, which is determined as usual, may include a little carbon introduced by the tar.

APPENDIX

APPENDIX

TABLE I.

ANALYTICAL CHARACTERISTICS OF CRUDE RUBBER SORTS.

THE number of wild rubbers figuring in trade as distinct sorts and sub-sorts runs to two hundred or over. Many of them, especially the African ones, are so ill-defined and variable that anything like a sound comprehensive classification based on quantitative data is impossible. The subjoined table gives no more than a generalized conspectus of some of the principal varieties. For fuller information the reader is referred to Weber's *The Chemistry of India Rubber* (London, 1902), now slightly out of date in some respects, and particularly to *Gummi-Kalender* (Berlin), 1913. For details of the several Congo sorts, see J. Liebschütz, *Gummi-Zeitung*, 21 (1907), p. 336.

W.L. = Percentage Washing Loss.

R. = Percentage of Resin in the washed and dried rubber.

A. = ,, Ash ,, ,, ,,

Designation.	W.L.	R.	A.
Para Hard Fine, Acre Para, Bolivian Fine (<i>Hevea</i>) . . .	16—21	2·5—3·5	0·2—0·4
Manaos Scrappy (<i>Hevea</i>) . . .	20—25	1·6—2·0	0·6—0·7
Para Negrohead, Sernamby (<i>Hevea</i>)	30—40	3—6	0·5—1·5
Cameta (<i>Hevea</i>)	45—50	1·4—1·8	0·5—0·8
Mattogrosso Virgin (<i>Hevea</i>) .	18—22	2·5—3·0	0·5—0·7

ANALYTICAL CHARACTERISTICS OF CRUDE RUBBER SORTS.—(contd.).

Designation.	W.L.	R.	A.
Mattogrosso Negrohead (<i>Hevea</i>)	20—25	1·5—2·0	1·5—2·0
Mollendo Fine (<i>Hevea</i>)	15—20	1·8—2·0	0·2—0·3
Mollendo Coarse (<i>Hevea</i>)	12—18	2·0—2·5	0·3—0·4
Caucho Ball, Peruvian Ball (<i>Castilloa</i>)	20—30	3—5	0·5—1·5
Maniçoba (<i>Manihot</i>)	25—35	2·8—3·0	3·0—4·5
Ceara Negrohead (<i>Manihot</i>)	20—30	4—5	1·0—1·5
Jequie (<i>Manihot</i>)	25—30	4·5—5·5	1·5—2·0
Mangabeira (<i>Hancornia</i>)	30—40	20—25	1·0—1·5
Ciudad Bolivar, Orinoco (<i>Hevea</i>)	15—20	7—8	0·4—0·7
Central American (<i>Castilloa</i>)	20—40	4—7	1·0—2·5
Guayule (<i>Parthenium</i>)	22—26	20—35	1·0—1·5
Sierra Leone, Conakry, Massai, Soudan (mostly <i>Landolphia</i>)	15—30	5—7	0·4—1·0
Bassam, Cape Coast, Accra, Lahou, Ivory Coast, Gold Coast (mostly <i>L.</i>)	25—40	7—11	0·7—1·0
Second Accra Lump, Saltpond, &c. (mostly <i>L.</i>)	30—40	29—38	1·4—2·0
Gambia, Bissao (mostly <i>L.</i>)	30—50	5—6	1·0—2·0
Gaboon, Loango, Ogowe, Congo Ball (mostly <i>L.</i>)	25—35	8—18	0·6—1·0
Lagos, Niger, Benin (<i>Landol-</i> <i>phia</i> and <i>Funtumia</i>)	30—40	10—25	0·3—0·7
Batanga, Cameroon (<i>L.</i> and <i>F.</i>)	25—35	10—15	0·5—1·0
Lower Congo, Wamba (mostly <i>L.</i>)	10—20	5—6	0·5—1·0
Angola, Loanda, Benguela (mostly <i>L.</i>)	25—40	5—7	1·0—2·0
Upper Congo sorts (mostly <i>L.</i>)	5—15	4—10	0·5—1·5
Mozambique, Beira (mostly <i>L.</i>)	7—15	5—8	0·1—0·8
Madagascar, Tamatave, Ma- junga (mostly <i>L.</i>)	20—30	7—10	0·2—0·5
Assam (<i>Ficus</i>)	15—35	5—11	0·5—1·0
Penang (<i>Ficus</i> , <i>Willughbeia</i> , &c.)	15—30	5—7	0·3—0·7
Borneo (mostly <i>Urceola</i>)	35—45	10—11	0·4—0·6
Java Plantation (<i>Ficus</i>)	1—2	5—6	0·3—0·4
Ceylon and Malayan Planta- tion (<i>Hevea</i>)	1—2	2·5—3·5	0·2—0·6
Plantation Rambong (<i>Ficus</i>)	1—2	7—8	0·2—0·3

TABLE II.

COMPARISON OF PRICES IN DIFFERENT MEASURES AND CURRENCIES.

The German rate of exchange is taken at £1 = 20 m. 40 pf.,
 the French rate at £1 = 25 fr. 25 c.

Per lb.	Per ton avoird.	Per kg.	Per kg.
s. d.	£ s. d.	M. pf.	Fr. c.
10 0	1,120 0 0	22 50	27 82
9 0	1,008 0 0	20 25	25 03
8 0	896 0 0	18 00	22 25
7 0	784 0 0	15 75	19 47
6 0	672 0 0	13 50	16 69
5 0	560 0 0	11 25	13 90
4 5½	498 1 3	10 00	12 37
4 0	448 0 0	9 00	11 12
3 7	402 7 10	8 08	10 00
3 0	336 0 0	6 75	8 35
2 0	224 0 0	4 50	5 56
1 0	112 0 0	2 25	2 78
11	102 13 4	2 06	2 55
10	93 6 8	1 87	2 32
9	84 0 0	1 69	2 08
8	74 13 4	1 50	1 85
7	65 6 8	1 31	1 62
6	56 0 0	1 12	1 39
5½	49 16 1	1 00	1 24
5	46 13 4	94	1 16
4½	40 4 9	81	1 00
4	37 6 8	75	93
3	28 0 0	56	70
2	18 13 4	37	46
1	9 6 8	19	23
	4 19 7	10	12
½	4 13 4	9	11
	4 0 6	8	10
¼	2 6 8	5	6

TABLE III.—CONVERSION OF CRUDE

If a crude rubber priced at A shillings per lb. has a Washing Loss of washing, &c., being ignored) is $\frac{100A}{100-B}$ shillings per lb. This value is

A	2 %	4 %	6 %	8 %	10 %	12 %	14 %	16 %
s. d.	s. d.	s. d.	s. d.	s. d.	s. d.	s. d.	s. d.	s. d.
6 0	6 1 $\frac{1}{2}$	6 3	6 4 $\frac{1}{2}$	6 6 $\frac{1}{2}$	6 8	6 10	6 11 $\frac{3}{4}$	7 1 $\frac{3}{4}$
5 10	5 11 $\frac{1}{2}$	6 1	6 2 $\frac{1}{2}$	6 4	6 5 $\frac{3}{4}$	6 7 $\frac{1}{2}$	6 9 $\frac{1}{2}$	6 11 $\frac{1}{2}$
5 8	5 9 $\frac{1}{2}$	5 10 $\frac{3}{4}$	6 0 $\frac{1}{2}$	6 2	6 3 $\frac{1}{2}$	6 5 $\frac{1}{2}$	6 7	6 9
5 6	5 7 $\frac{1}{2}$	5 8 $\frac{3}{4}$	5 10 $\frac{1}{4}$	5 11 $\frac{3}{4}$	6 1 $\frac{1}{2}$	6 3	6 4 $\frac{3}{4}$	6 6 $\frac{1}{2}$
5 4	5 5 $\frac{1}{4}$	5 6 $\frac{3}{4}$	5 8	5 9 $\frac{1}{2}$	5 11	6 0 $\frac{3}{4}$	6 2 $\frac{1}{2}$	6 4 $\frac{1}{4}$
5 2	5 3 $\frac{1}{4}$	5 4 $\frac{1}{2}$	5 6	5 7 $\frac{1}{2}$	5 9	5 10 $\frac{1}{2}$	6 0	6 1 $\frac{1}{4}$
5 0	5 1 $\frac{1}{4}$	5 2 $\frac{1}{2}$	5 3 $\frac{3}{4}$	5 5 $\frac{1}{4}$	5 6 $\frac{3}{4}$	5 8 $\frac{1}{4}$	5 9 $\frac{3}{4}$	5 11 $\frac{1}{2}$
4 10	4 11 $\frac{1}{4}$	5 0 $\frac{1}{2}$	5 1 $\frac{1}{4}$	5 3	5 4 $\frac{1}{2}$	5 6	5 7 $\frac{1}{2}$	5 9
4 8	4 9	4 10 $\frac{1}{4}$	4 11 $\frac{1}{2}$	5 1	5 2 $\frac{1}{4}$	5 3 $\frac{1}{2}$	5 5	5 6 $\frac{1}{2}$
4 6	4 7	4 8 $\frac{1}{4}$	4 9 $\frac{1}{2}$	4 10 $\frac{3}{4}$	5 0	5 1 $\frac{1}{2}$	5 2 $\frac{3}{4}$	5 4 $\frac{1}{2}$
4 4	4 5	4 6 $\frac{1}{4}$	4 7 $\frac{1}{4}$	4 8 $\frac{1}{2}$	4 9 $\frac{3}{4}$	4 11 $\frac{3}{4}$	5 0 $\frac{1}{2}$	5 2
4 2	4 3	4 4	4 5 $\frac{1}{4}$	4 6 $\frac{1}{4}$	4 7 $\frac{1}{2}$	4 8 $\frac{3}{4}$	4 10	4 11 $\frac{1}{2}$
4 0	4 1	4 2	4 3	4 4 $\frac{1}{2}$	4 5 $\frac{1}{4}$	4 6 $\frac{1}{2}$	4 7 $\frac{3}{4}$	4 9
3 10	3 11	4 0	4 1	4 2	4 3 $\frac{1}{4}$	4 4 $\frac{1}{2}$	4 5 $\frac{1}{2}$	4 6 $\frac{3}{4}$
3 8	3 9	3 10	3 10 $\frac{3}{4}$	3 11 $\frac{3}{4}$	4 1	4 2	4 3 $\frac{1}{4}$	4 4 $\frac{1}{2}$
3 6	3 7	3 7 $\frac{3}{4}$	3 8 $\frac{3}{4}$	3 9 $\frac{1}{2}$	3 10 $\frac{3}{4}$	3 11 $\frac{3}{4}$	4 0 $\frac{3}{4}$	4 2
3 4	3 4 $\frac{3}{4}$	3 5 $\frac{3}{4}$	3 6 $\frac{1}{2}$	3 7 $\frac{1}{2}$	3 8 $\frac{1}{2}$	3 9 $\frac{1}{2}$	3 10 $\frac{1}{2}$	3 11 $\frac{1}{2}$
3 2	3 2 $\frac{3}{4}$	3 3 $\frac{1}{2}$	3 4 $\frac{1}{2}$	3 5 $\frac{1}{4}$	3 6 $\frac{1}{4}$	3 7 $\frac{1}{4}$	3 8	3 9 $\frac{1}{4}$
3 0	3 0 $\frac{1}{4}$	3 1 $\frac{1}{2}$	3 2 $\frac{1}{4}$	3 3	3 4	3 5	3 6	3 7
2 10	2 10 $\frac{3}{4}$	2 11 $\frac{1}{2}$	3 0	3 1	3 1 $\frac{1}{2}$	3 2 $\frac{1}{2}$	3 3 $\frac{1}{2}$	3 4 $\frac{1}{2}$
2 8	2 8 $\frac{3}{4}$	2 9 $\frac{1}{2}$	2 10	2 10 $\frac{3}{4}$	2 11 $\frac{1}{2}$	3 0 $\frac{1}{4}$	3 1 $\frac{1}{4}$	3 2
2 6	2 6 $\frac{1}{2}$	2 7 $\frac{1}{4}$	2 8	2 8 $\frac{1}{2}$	2 9 $\frac{1}{2}$	2 10	2 11	2 11 $\frac{3}{4}$
2 4	2 4 $\frac{1}{2}$	2 5	2 5 $\frac{3}{4}$	2 6 $\frac{1}{2}$	2 7	2 7 $\frac{3}{4}$	2 8 $\frac{1}{2}$	2 9 $\frac{1}{4}$
2 2	2 2 $\frac{1}{2}$	2 3	2 3 $\frac{1}{2}$	2 4 $\frac{1}{4}$	2 5	2 5 $\frac{1}{2}$	2 6 $\frac{1}{4}$	2 7
2 0	2 0 $\frac{1}{2}$	2 1	2 1 $\frac{1}{2}$	2 2	2 2	2 2 $\frac{1}{2}$	2 3 $\frac{1}{4}$	2 4 $\frac{1}{2}$
1 10	1 10 $\frac{1}{2}$	1 11	1 11 $\frac{1}{2}$	2 0	2 0 $\frac{1}{2}$	2 1	2 1 $\frac{1}{2}$	2 2 $\frac{1}{4}$
1 8	1 8 $\frac{1}{2}$	1 8 $\frac{3}{4}$	1 9 $\frac{1}{4}$	1 9 $\frac{3}{4}$	1 10 $\frac{1}{4}$	1 10 $\frac{3}{4}$	1 11 $\frac{1}{4}$	1 11 $\frac{3}{4}$
1 6	1 6 $\frac{1}{2}$	1 6 $\frac{3}{4}$	1 7 $\frac{1}{4}$	1 7 $\frac{1}{2}$	1 8	1 8 $\frac{1}{2}$	1 9	1 9 $\frac{1}{2}$
1 4	1 4 $\frac{1}{4}$	1 4 $\frac{3}{4}$	1 5	1 5 $\frac{1}{2}$	1 5 $\frac{3}{4}$	1 6 $\frac{1}{4}$	1 6 $\frac{1}{2}$	1 7
1 2	1 2 $\frac{1}{4}$	1 2 $\frac{1}{2}$	1 2 $\frac{3}{4}$	1 3 $\frac{1}{4}$	1 3 $\frac{1}{2}$	1 4	1 4 $\frac{1}{4}$	1 4 $\frac{3}{4}$
1 0	1 0 $\frac{1}{4}$	1 0 $\frac{1}{2}$	1 0 $\frac{3}{4}$	1 1	1 1 $\frac{1}{4}$	1 1 $\frac{1}{2}$	1 2	1 2 $\frac{1}{4}$
10	10 $\frac{1}{4}$	10 $\frac{1}{2}$	10 $\frac{3}{4}$	11	11	11 $\frac{1}{4}$	11 $\frac{1}{2}$	11 $\frac{3}{4}$
8	—	8 $\frac{1}{4}$	8 $\frac{1}{2}$	8 $\frac{3}{4}$	9	9	9 $\frac{1}{4}$	9 $\frac{1}{2}$
6	—	6 $\frac{1}{4}$	6 $\frac{1}{2}$	6 $\frac{3}{4}$	6 $\frac{3}{4}$	6 $\frac{3}{4}$	7	7 $\frac{1}{4}$

INTO WASHED RUBBER PRICES.

B per cent., then the actual cost of the clean dry rubber (cost of worked out in the subjoined table for a series of values of *A* and *B*.

18 %	20 %	22 %	24 %	26 %	28 %	30 %	32 %	<i>A</i>
s. d. 7 4	s. d. 7 6	s. d. 7 8½	s. d. 7 10½	s. d. 8 1½	s. d. 8 4	s. d. 8 7	s. d. 8 10	s. d. 6 0
7 1½	7 3½	7 5½	7 8	7 10½	8 1½	8 4	8 7	5 10
6 11	7 1	7 3½	7 5½	7 8	7 10½	8 1	8 4	5 8
6 8½	6 10½	7 0½	7 2½	7 5½	7 7½	7 10½	8 1	5 6
6 6	6 8	6 10	7 0½	7 2½	7 5	7 7½	7 10	5 4
6 3½	6 5½	6 7½	6 9½	6 11½	7 2	7 4½	7 7½	5 2
6 1½	6 3	6 5	6 7	6 9	6 11½	7 1½	7 4½	5 0
5 10½	6 0½	6 2½	6 4½	6 6½	6 8½	6 11	7 1½	4 10
5 8½	5 10	5 11½	6 1½	6 3½	6 6	6 8	6 10½	4 8
5 6	5 7½	5 9½	5 11	6 1	6 3	6 5	6 7½	4 6
5 3½	5 5	5 6½	5 8½	5 10½	6 0½	6 2½	6 4½	4 4
5 1	5 2½	5 4	5 5½	5 7½	5 9½	5 11½	6 1½	4 2
4 10½	5 0	5 1½	5 3	5 5	5 6½	5 8½	5 10½	4 0
4 8	4 9½	4 11	5 0½	5 2½	5 3½	5 5½	5 7½	3 10
4 5½	4 7	4 8½	4 10	4 11½	5 1	5 3	5 4½	3 8
4 3½	4 4½	4 5½	4 7½	4 8½	4 10½	5 0	5 1½	3 6
4 0½	4 2	4 3½	4 4½	4 6	4 7½	4 9	4 10½	3 4
3 10½	3 11½	4 0½	4 2	4 3½	4 4½	4 6½	4 8	3 2
3 8	3 9	3 10½	3 11½	4 0½	4 2	4 3½	4 5	3 0
3 5½	3 6½	3 7½	3 8½	3 10	3 11½	4 0½	4 2	2 10
3 3	3 4	3 5	3 6	3 7½	3 8½	3 9½	3 11	2 8
3 0½	3 1½	3 2½	3 3½	3 4½	3 5½	3 6½	3 8	2 6
2 10	2 11	3 0	3 0½	3 1½	3 3	3 4	3 5	2 4
2 7½	2 8½	2 9½	2 10½	2 11	3 0	3 1	3 2½	2 2
2 5½	2 6	2 6½	2 7½	2 8½	2 9½	2 10½	2 11½	2 0
2 2½	2 3½	2 4½	2 5	2 5½	2 6½	2 7½	2 8½	1 10
2 0½	2 1	2 1½	2 2½	2 3	2 3½	2 4½	2 5½	1 8
1 10	1 10½	1 11	1 11½	2 0½	2 1	2 1½	2 2½	1 6
1 7½	1 8	1 8½	1 9	1 9½	1 10½	1 11	1 11½	1 4
1 5	1 5½	1 6	1 6½	1 7	1 7½	1 8	1 8½	1 2
1 2½	1 3	1 3½	1 3½	1 4½	1 4½	1 5	1 5½	1 0
1 0½	1 0½	1 0½	1 1	1 1½	1 2	1 2½	1 2½	10
9½	10	10½	10½	10¾	11	11½	11½	8
7½	7½	7½	8	8	8½	8½	8½	6

TABLE III.—CONVERSION OF CRUDE

If a crude rubber priced at A shillings per lb. has a Washing Loss of washing, &c., being ignored) is $\frac{100A}{100-B}$ shillings per lb. This value is

A	34 %	36 %	38 %	40 %	42 %	44 %	46 %
s. d.							
6 0	9 1	9 4½	9 8	10 0	10 4	10 8½	11 1½
5 10	8 10	9 1½	9 5	9 8½	10 0½	10 5	10 9½
5 8	8 7	8 10½	9 1½	9 5½	9 9½	10 1½	10 6
5 6	8 4	8 7	8 10½	9 2	9 5½	9 10	10 2
5 4	8 1	8 4	8 7	8 10½	9 2½	9 6½	9 10½
5 2	7 10	8 1	8 4	8 7½	8 11	9 2½	9 6½
5 0	7 7	7 9½	8 0½	8 4	8 7½	8 11	9 3
4 10	7 4	7 6½	7 9½	8 0½	8 4	8 7½	8 11½
4 8	7 1	7 3½	7 6½	7 9½	8 0½	8 4	8 7½
4 6	6 9½	7 0½	7 3	7 6	7 9	8 0½	8 4
4 4	6 6½	6 9½	6 11½	7 2½	7 5½	7 9	8 0½
4 2	6 4½	6 6	6 8½	6 11½	7 1½	7 5½	7 7
4 0	6 0½	6 3	6 5½	6 8	6 10½	7 1½	7 5
3 10	5 9½	5 11½	6 2½	6 4½	6 7½	6 10	7 1
3 8	5 6½	5 8½	5 11	6 1½	6 4	6 6½	6 9½
3 6	5 3½	5 5½	5 7½	5 10	6 0½	6 3	6 5½
3 4	5 0½	5 2½	5 4½	5 6½	5 9	5 11½	6 2
3 2	4 9½	4 11½	5 1½	5 3½	5 5½	5 8	5 10½
3 0	4 6½	4 8½	4 10	5 0	5 2	5 4½	5 6½
2 10	4 3½	4 5	4 7	4 8½	4 10½	5 0½	5 3
2 8	4 0½	4 2	4 3½	4 5½	4 7½	4 9	4 11½
2 6	3 9½	3 11	4 0½	4 2	4 3½	4 5½	4 7½
2 4	3 6½	3 7½	3 9	3 10½	4 0½	4 2	4 4
2 2	3 3½	3 4½	3 6	3 7½	3 8½	3 10½	4 0
2 0	3 0½	3 1½	3 2½	3 4	3 5½	3 7	3 8½
1 10	2 9½	2 10½	2 11½	3 0½	3 2	3 3½	3 4½
1 8	2 6½	2 7½	2 8½	2 9½	2 10½	2 11½	3 1
1 6	2 3½	2 4	2 5	2 6	2 7	2 8½	2 9½
1 4	2 0½	2 1	2 1½	2 2½	2 3½	2 4½	2 5½
1 2	1 9½	1 10	1 10½	1 11½	2 0½	2 1	2 2
1 0	1 6	1 6½	1 7½	1 8	1 8½	1 9½	1 10½
10	1 3	1 3½	1 4	1 4½	1 5½	1 5½	1 6½
8	1 0	1 0½	1 1	1 1½	1 1½	1 2½	1 2½
6	9	9½	9¾	10	10½	10½	11

INTO WASHED RUBBER PRICES—(continued).

B per cent., then the actual cost of the clean dry rubber (cost of worked out in the subjoined table for a series of values of *A* and *B*.

48 %	50 %	52 %	54 %	56 %	58 %	60 %	<i>A.</i>
<i>s.</i> <i>d.</i>							
11 6½	12 0	12 6	13 0½	13 7½	14 3½	15 0	6 0
11 2½	11 8	12 1½	12 8	13 3	13 10½	14 7	5 10
10 10½	11 4	11 9½	12 4	12 10½	13 6	14 2	5 8
10 7	11 0	11 5½	11 11½	12 6	13 1	13 9	5 6
10 3	10 8	11 1½	11 7	12 1½	12 8½	13 4	5 4
9 11½	10 4	10 9	11 2½	11 9	12 3½	12 11	5 2
9 7½	10 0	10 5	10 10½	11 4½	11 11	12 6	5 0
9 3½	9 8	10 1	10 6	11 0	11 6	12 1	4 10
8 11½	9 4	9 8½	10 1½	10 7½	11 1½	11 8	4 8
8 8	9 0	9 4½	9 11½	10 2½	10 8½	11 3	4 6
8 4	8 8	9 0½	9 5	9 10	10 3½	10 10	4 4
8 0½	8 4	8 8	9 0½	9 5½	9 11	10 5	4 2
7 8½	8 0	8 4	8 8½	9 1	9 6½	10 0	4 0
7 4½	7 8	8 0	8 4	8 8½	9 1½	9 7	3 10
7 0½	7 4	7 7½	7 11½	8 4	8 8½	9 2	3 8
6 9	7 0	7 3½	7 7½	7 10½	8 4	8 9	3 6
6 4½	6 8	6 11½	7 3	7 7	7 11½	8 4	3 4
6 1	6 4	6 6½	6 10½	7 2½	7 6½	7 11	3 2
5 9½	6 0	6 3	6 6½	6 9½	7 2½	7 6	3 0
5 5½	5 8	5 10½	6 2	6 5½	6 9	7 1	2 10
5 1½	5 4	5 6½	5 9½	6 0½	6 4½	6 8	2 8
4 9½	5 0	5 2½	5 5½	5 8½	5 11½	6 3	2 6
4 6	4 8	4 10½	5 1	5 4½	5 6½	5 10	2 4
4 2	4 4	4 6½	4 8½	4 11	5 2	5 5	2 2
3 10½	4 0	4 2	4 4½	4 6½	4 9	5 0	2 0
3 6½	3 8	3 9½	3 11½	4 2	4 4½	4 7	1 10
3 2½	3 4	3 5½	3 7½	3 9½	3 11½	4 2	1 8
2 10½	3 0	3 1½	3 3	3 5	3 7	3 9	1 6
2 6½	2 8	2 9½	2 10½	3 0½	3 2	3 4	1 4
2 3	2 4	2 5½	2 6½	2 7½	2 9½	2 11	1 2
1 11	2 0	2 1	2 2	2 3½	2 4½	2 6	1 0
1 7½	1 8	1 8½	1 9½	1 10½	1 11½	2 1	8 8
1 3½	1 4	1 4½	1 5½	1 6½	1 7	1 3	6 6
1 1½	1 0	1 0½	1 1	1 1½	1 2½	1 3	

TABLE IV.

CORRESPONDING TEMPERATURES AND SATURATED STEAM PRESSURES.

1 Atmosphere = 1·033 kg. per sq. cm. = 14·72 lb. per sq. in.

De-grees C.	Degrees F.	Atmo-spheres.	Pounds per sq. inch.	De-grees C.	Degrees F.	Atmo-spheres.	Pounds per sq. inch.
100	212·0	1·00	14·7	141	285·8	3·68	54·2
101	213·8	1·03	15·2	142	287·6	3·78	55·7
102	215·6	1·07	15·7	143	289·4	3·89	57·3
103	217·4	1·11	16·3	144	291·2	4·00	58·9
104	219·2	1·15	16·9	145	293·0	4·11	60·5
105	221·0	1·19	17·5	146	294·8	4·22	62·2
106	222·8	1·23	18·1	147	296·6	4·34	63·9
107	224·6	1·27	18·7	148	298·4	4·46	65·7
108	226·4	1·31	19·3	149	300·2	4·58	67·5
109	228·2	1·36	20·0	150	302·0	4·71	69·4
110	230·0	1·41	20·7	151	303·8	4·84	71·3
111	231·8	1·46	21·4	152	305·6	4·97	73·2
112	233·6	1·51	22·2	153	307·4	5·10	75·1
113	235·4	1·56	23·0	154	309·2	5·24	77·1
114	237·2	1·62	23·8	155	311·0	5·38	79·2
115	239·0	1·67	24·6	156	312·8	5·52	81·3
116	240·8	1·72	25·4	157	314·6	5·67	83·4
117	242·6	1·78	26·2	158	316·4	5·82	85·6
118	244·4	1·84	27·1	159	318·2	5·97	87·8
119	246·2	1·90	28·0	160	320·0	6·12	90·1
120	248·0	1·96	28·9	161	321·8	6·28	92·4
121	249·8	2·02	29·8	162	323·6	6·44	94·8
122	251·6	2·08	30·7	163	325·4	6·60	97·2
123	253·4	2·15	31·7	164	327·2	6·77	99·7
124	255·2	2·22	32·7	165	329·0	6·94	102·2
125	257·0	2·29	33·7	166	330·8	7·11	104·8
126	258·8	2·36	34·8	167	332·6	7·29	107·4
127	260·6	2·43	35·9	168	334·4	7·47	110·0
128	262·4	2·51	37·0	169	336·2	7·65	112·6
129	264·2	2·59	38·1	170	338·0	7·84	115·3
130	266·0	2·67	39·3	171	339·8	8·03	118·1
131	267·8	2·75	40·5	172	341·6	8·23	121·0
132	269·6	2·83	41·7	173	343·4	8·43	123·9
133	271·4	2·92	43·0	174	345·2	8·63	126·9
134	273·2	3·01	44·3	175	347·0	8·84	130·0
135	275·0	3·10	45·6	176	348·8	9·05	133·1
136	276·8	3·19	47·0	177	350·6	9·26	136·3
137	278·6	3·28	48·4	178	352·4	9·48	139·5
138	280·4	3·38	49·8	179	354·2	9·70	142·8
139	282·2	3·48	51·2	180	356·0	9·93	146·1
140	284·0	3·58	52·7				

TABLE V.

PHYSICAL CONSTANTS OF VARIOUS LIQUIDS.

Substance.	Boiling point, Degrees C.	Sp. Gr. at 15°.	Coeff. of Expansion at ord. temp.
Bromine	63	3·15	0·00116
Sulphur Chloride	137	1·68	0·00100
Carbon Disulphide	46	1·27	0·00120
Pentane	37	0·630	0·00160
Hexane	70	0·664	0·00144
Heptane	98	0·688	0·00121
Octane	125	0·703	0·00112
Nonane	149	0·721	—
Decane	173	0·734	0·00101
Mineral Naphtha	70—150	0·74—0·76	0·0012
Petroleum (Lamp Oil)	150—300	0·79—0·82	0·0010
Benzene	80	0·880	0·00124
Toluene	110	0·871	0·00110
o-Xylene	142	0·878	0·00097
m-Xylene	140	0·869	0·00100
p-Xylene	138	0·864	0·00101
Pseudocumene	170	0·872	0·00095
Mesitylene	164	0·865	—
Solvent Naphtha	125—160	0·86—0·87	0·0010
Nitrobenzene	205	1·19	—
Pinene (Turpentine)	160	0·860	0·00097
Pyridine	117	0·986	—
Carbon Tetrachloride	77	1·60	0·00124
Chloroform	61	1·49	0·00127
Dichlorethylene	55	1·25	—
Trichlorethylene	88	1·47	—
Pentachlorethane	159	1·70	0·00091
Epichlorhydrin	116	1·19	—
Ethyl Alcohol	78	0·794	0·00110
Do. 95 per cent.	—	0·816	0·00108
Do. 90 ,,"	—	0·833	0·00105
Methyl Alcohol	66	0·797	0·00126
Diethyl Ether	35	0·720	0·00161
Acetone	56	0·795	0·00149
Ethyl Acetate	77	0·895	0·00138
Amyl Acetate	148	0·865	0·00116
Acetic Acid (glacial)	119	1·056	0·00107
Glycerine	290	1·267	0·00051
Fatty Oils	—	0·915—0·930	0·0007

TABLE VI.

SPECIFIC VOLUME (INVERSE DENSITY) OF WATER FROM 0° TO 31° REFERRED TO WATER AT 4°.

In making use of this table for applying corrections, it is convenient to add or subtract parts per 10,000 to or from the quantity under correction, as one would add or subtract a percentage. A comma is accordingly inserted between the fourth and fifth place of decimals.

Temperature.	Specific Volume.	Temperature.	Specific Volume.
Degrees. 0	1·0001,3	Degrees. 16	1·0010,3
1	1·0000,7	17	1·0012,0
2	1·0000,3	18	1·0013,8
3	1·0000,1	19	1·0015,7
4	1·0000,0	20	1·0017,7
5	1·0000,1	21	1·0018,5
6	1·0000,3	22	1·0022,1
7	1·0000,7	23	1·0024,4
8	1·0001,3	24	1·0026,8
9	1·0001,9	25	1·0029,4
10	1·0002,7	26	1·0032,0
11	1·0003,7	27	1·0034,7
12	1·0004,8	28	1·0037,5
13	1·0005,9	29	1·0040,5
14	1·0007,3	30	1·0043,5
15	1·0008,7	31	1·0046,5

TABLE VII.
ANALYTICAL FACTORS OF CONVERSION.

Element.	Found.	Required.	Factor.
Aluminium	Al_2O_3	Al	0·5303
Antimony	SbO_2	Sb	0·7897
	Sb_2S_3	Sb	0·7142
Barium	BaSO_4	BaO	0·6571
	BaSO_4	BaCO_3	0·8455
Bromine	AgBr	Br	0·4255
Calcium	CaO	CaCO_3	1·7843
	CaO	Ca(OH)_2	1·3212
	CaO	CaSO_4	2·4271
	CaO	$\text{CaSO}_4 \cdot 2\text{Aq}$	2·7481
	CO_2	CaCO_3	2·2750
Carbon	CO_2	C	0·2727
Chlorine	AgCl	Cl	0·2472
Iron	Fe_2O_3	Fe	0·6996
Magnesium	$\text{Mg}_2\text{P}_2\text{O}_7$	MgO	0·3624
	MgO	MgCO_3	0·2090
	CO_2	MgCO_3	0·1917
	MgO	Mg	0·6036
Lead	PbSO_4	PbO	0·7357
	PbS	PbO	0·9328
	PbO	Pb	0·9282
	S	PbS	7·4536
Mercury	Hg	HgS	1·1603
	S	HgS	7·2383
Sulphur	BaSO_4	S	0·1373
	BaSO_4	SO_3	0·3429
	BaSO_4	SO_4	0·4114
	BaSO_4	H_2SO_4	0·4201
Tin	SnO_2	Sn	0·7880
Zinc	ZnO	ZnS	1·1973
	ZnO	Zn	0·8034
	S	ZnS	3·0372

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